INVESTIGATION OF THE ROLE OF CHLORINATED BENZENES AND PHENOLS IN PCDD/F FORMATION

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APPROVED BY:

ABSTRACT

INVESTIGATION OF THE ROLE OF CHLORINATED BENZENES AND PHENOLS IN PCDD/F FORMATION

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University of Dayton, August 2000

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The discovery of emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F or simply "dioxins") from waste incinerators and other thermal processes has caused a great deal of concern and has hindered the acceptance of incineration as a widespread means of waste treatment. It is necessary to gain a fundamental understanding of the global mechanism of formation in order to find ways to adjust combustion parameters so that PCDD/F emissions can be minimized.

In this work, chlorination of two key precursors to PCDD/F formation, benzene and phenol, was studied on a model fly ash surface. Experiments were conducted using the System for Thermal Diagnostics Studies (STDS), which consists of a high-temperature flow reactor coupled with an in-line gas chromatograph/ mass spectrometer (GC/ MS) designed to simulate the reaction conditions in an incinerator post-flame zone. It was found that both precursors chlorinated readily from 300 to 500°C, and there was significant inter-conversion between chlorinated benzenes and chlorinated phenols. Chlorination occurred even at low residence times (25 ms). To bypass the complexities associated with surface effects, it was decided to study the mechanism of gas-phase interaction of chlorinated benzenes and phenols in relation to PCDD/F formation. The 2-chlorophenol, 2-chloroanisole, and monochlorobenzene experiments showed that the concentration of radicals present in the oxidation system has a significant effect on the PCDD/F product distribution and ultimately the PCDD: PCDF ratio. Monochlorobenzene also produced a significant amount of phenols and produced PCDD/F in lower yields than 2-chlorophenol, suggesting that the most formation of PCDD/F from chlorobenzenes passes through a phenol intermediate.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F or simply "dioxins") are a class of 210 isomeric species that are known to cause adverse health effects in humans and animals [1]. Their ability to initiate cancer, severe skin disorders, and reproductive disorders originally caused concern over their exposure as a contaminant in commercial chemicals including polychlorinated biphenyls, Agent Orange, and synthetic creosote. However, it was the discovery of their presence in the effluent of municipal waste incinerators (MWI) in the late 70's and early 80's and the realization that broad segments of the population are exposed to these chemicals that raised the most concern [2]. Subsequent research has shown that combustion or thermal processes that contain a source of chlorine emit measurable quantities of PCDD/F, polychlorinated biphenyls (PCB), and polychlorinated naphthalenes (PCN). It is now generally accepted that combustion is the major source of PCDD/F, PCB, and PCN in the environment. The total annual U.S. air emissions of dioxin and “dioxin-like” compounds from all known sources is estimated to be about 3 kg Toxic Equivalency (kg TEQ/yr) per year as of 1995, almost entirely from combustion sources [3]. Anthropogenic emissions are thought to be about an order of magnitude greater than forest fires, which is the largest known non-anthropogenic source [3]. Common combustion sources such as medical waste incinerators, municipal solid waste combustors, cement kilns and boilers, residential wood burning, and industrial wood burning are among the major characterized anthropogenic sources. However, many other combustion and thermal sources, e.g. chlorinated hydrocarbon manufacturing operations, secondary copper smelters, ferrous metal foundries, Kraft black liquor boilers, diesel fuel combustion, and petroleum combustion, may make a significant contribution to the environment's dioxin and “dioxin-like” compound burden. A list of estimated contributions from various sources is shown in Table 1.1.

Table 1.1: Estimates of PCDD/F emissions from various sources (1994).

Emission Source	grams TEQ/ year
Sewage sludge incineration	10-52
Municipal waste incineration (MWI)	1800-9000
Hazardous waste incineration	11-110
Hospital waste incineration	1600-16000
Cement kilns	110-1100
Metal smelting/refining	75-745
Drum and barrel reclamation	0.5-5.0
Vehicle fuel combustion	27-270
Combustion of wood	113-1063
Forest fires	27-270
Kraft black liquor boilers	0.9-4.3

The USEPA's dioxin reassessment has concluded that the background levels of PCDD/F in the environment and human body are just below the threshold of significant health effects and that increases, or even continued emissions at current levels, will result in observable, adverse human health effects. Consequently, the EPA has launched a Combustion Strategy designed to reduce the emissions of dioxins and dioxin-like compounds from combustion sources. The initial focus has been on municipal waste combustors and facilities that burn hazardous wastes. However, many other thermal and combustion sources are now the target of potential regulation [4].

The current approach of the combustion strategy to reduce the environmental burden of dioxins is to either require the addition of costly control devices or to eliminate the source from existence. This is clearly an economically infeasible approach for the large majority of our nation's combustion and thermal processes. Thus to continue to allow the use of combustion while reducing PCDD/F, PCB, and PCN emissions, we must find methods to prevent their formation (the structures of these dioxin and dioxin- like compounds are shown in Figure 1.1). Because there are so many combustion sources, developing a prevention strategy for one source alone will not be successful. Thus, there is a need to develop a better understanding of the mechanism of formation of these pollutants that can lead to development of pollutant formation control strategies that are based on a modification of combustion parameters. Such control techniques will be applicable to a wide range of sources.

The approach taken here is to examine particular steps in the pathways of PCDD/F formation from a prevention perspective. Since all aspects of the global mechanism of formation are not fully understood, it is necessary to study certain elementary steps that are essential to PCDD/F formation. One such key step is the chlorination of known precursors. The literature has reported the involvement of nearly every conceivable organic halogen compound in PCDD/F formation under suitable laboratory conditions, but many of these may be of no consequence in actual industrial processes. It is well documented that chlorobenzenes and chlorophenols (present in significant quantities in MWI flue gas) readily undergo molecular growth reactions to form dioxins and act as intermediates to PCDD/F formation from small aliphatic precursors [5-7]. Although significant studies have been performed concerning the mechanism of formation of PCDD/F from these precursors, the inter-conversion of benzene and phenol and their competitive reactions have not been investigated. The objective of this study is to examine the competitive chlorination of benzene and phenol on model fly ash surfaces and in the gas phase, and to examine the subsequent formation of PCDD/F from the chlorinated precursors.

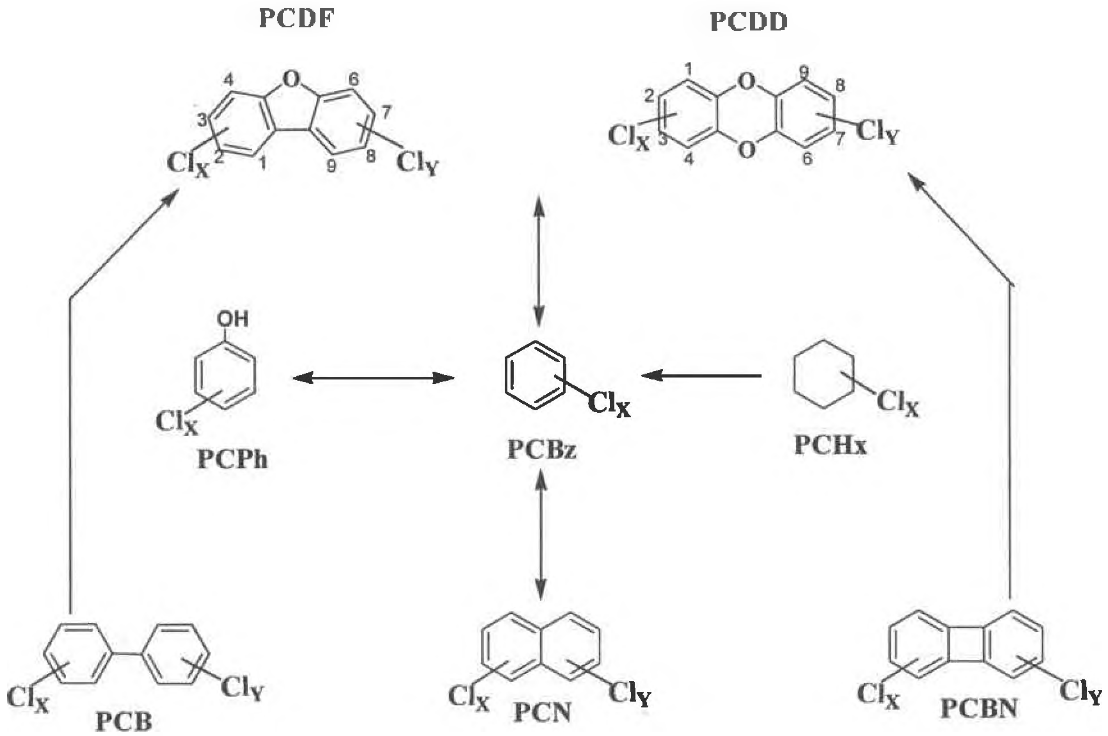


Figure 1.1. Structures of dioxin and "dioxin-like" compounds and their aromatic precursors (chlorophenols, chlorobenzenes, and chlorocyclohexanes).

CHAPTER II

BACKGROUND

Several origins of PCDD/F emissions from combustion processes have been examined. The three widely accepted pathways of formation are: (1) synthesis of native elemental carbon present in the fly ash or soot to form PCDD/F, (2) formation of PCDD/F from homogeneous gas- phase reactions of organic precursors, and (3) heterogeneous surface catalyzed reactions of organic precursors.

The first pathway is referred to as *de novo* synthesis, where chlorine, oxygen, hydrogen, and macromolecular carbon in the fly ash matrix are combined in the presence of gas-phase oxygen to form aromatic precursors and dioxin like compounds. This occurs in the low temperature regions of the post-combustion zone (200-500°C). *De novo* formation of PCDD/F has been examined by several researchers. Simply heating fly ash in the presence of air from 250-500°C has resulted in the formation of dioxins, although in yields too small to account for emissions measured in full scale MWI [8,9]. However, when effluent gases from an actual combustion source are passed over fly ash (the effluent contains HCl, oxygen, and catalytic metals), yields are comparable with MWI field data [8, 10]. There is evidence that *de novo* formation is caused by combustion radicals that attack the soot or fly ash matrix, forming small precursors which undergo molecular growth reactions to form PCDD/F. An illustration of *de novo* synthesis is shown in Figure 2.1.

Dioxins and related compounds can also be formed from benzene, phenol, and aliphatic hydrocarbon precursors by homogeneous gas- phase reactions in high temperature regions of the post-combustion zone (500- 900 °C). An early kinetic analysis by Shaub & Tsang has suggested that the gas- phase formation is much slower and predicts the homogeneous PCDD/F yields in incinerators to be of minor significance [11]. However, there is convincing evidence from incinerator test data of significant formation of PCDD/F in high-temperature combustion gas [12]. The mechanism and kinetics of the process were again examined by Sidhu et al., and it was suggested that homogeneous gas- phase formation could contribute a significant amount of PCDD/F formation [13].

Surface catalyzed reactions of organic precursors in the low temperature region of the post-combustion zone (200-450°C) to form PCDD/F is also well documented. The precursors are formed as a result of *de novo* synthesis from soot or as products of incomplete combustion of the fuel. Karasek and Dickson showed that pentachlorophenol (PCP) can be condensed on fly ash surface to form PCDD/F [14]. Isotopically labeled PCP was passed over an empty tube, ground firebrick, and fly ash in temperatures of 150-400°C. Empty tube and firebrick (non-catalytic surface) runs resulted in little or no isotopically labeled PCDD/F products. But the fly ash surface produced appreciable yields of labeled PCDD/F products in the temperature range of 250-350°C. It was concluded that metallic constituents in the fly ash were catalyzing the formation of dioxins from chlorophenols. More recent experiments show evidence of classic gas-solid equilibrium behavior between tetrachlorophenol (TCP) on fly ash: the chlorophenol adsorbs to the fly ash surface, reacts to form PCDD/F, and the products desorb back into the gas-phase, followed by re-adsorption of TCP [15]. The TCP was found to follow a Freundlich adsorption isotherm due to the non-ideal nature of the fly ash surface. PCDD/F formation on model fly ash surfaces has also been examined. For example, acetylene, a common combustor effluent, was found to chlorinate and condense readily on a silica-based surface coated with $CuCl_2$ [7]. Products observed were chlorinated aliphatics, chlorinated aromatics, and PCDD/F. It is now generally accepted that metallic constituents in the fly ash matrix (Fe, Cu complexes) are responsible for catalyzing condensation reactions of precursors to form PCDD/F. The mechanism of formation of PCDD/F from chemically similar precursors is shown in Figure 2.2.

The mechanistic situation is complicated by the evidence that there is no one pathway that is dominant. Isotopic studies have usually concluded that PCDD/F is formed as a combination of *de novo* synthesis, surface-catalyzed reactions, and gas-phase molecular growth reactions. It is likely that a unified pathway exists that incorporates these three separate origins. Such a global route to PCDD/F formation is outlined in Figure 2.3.

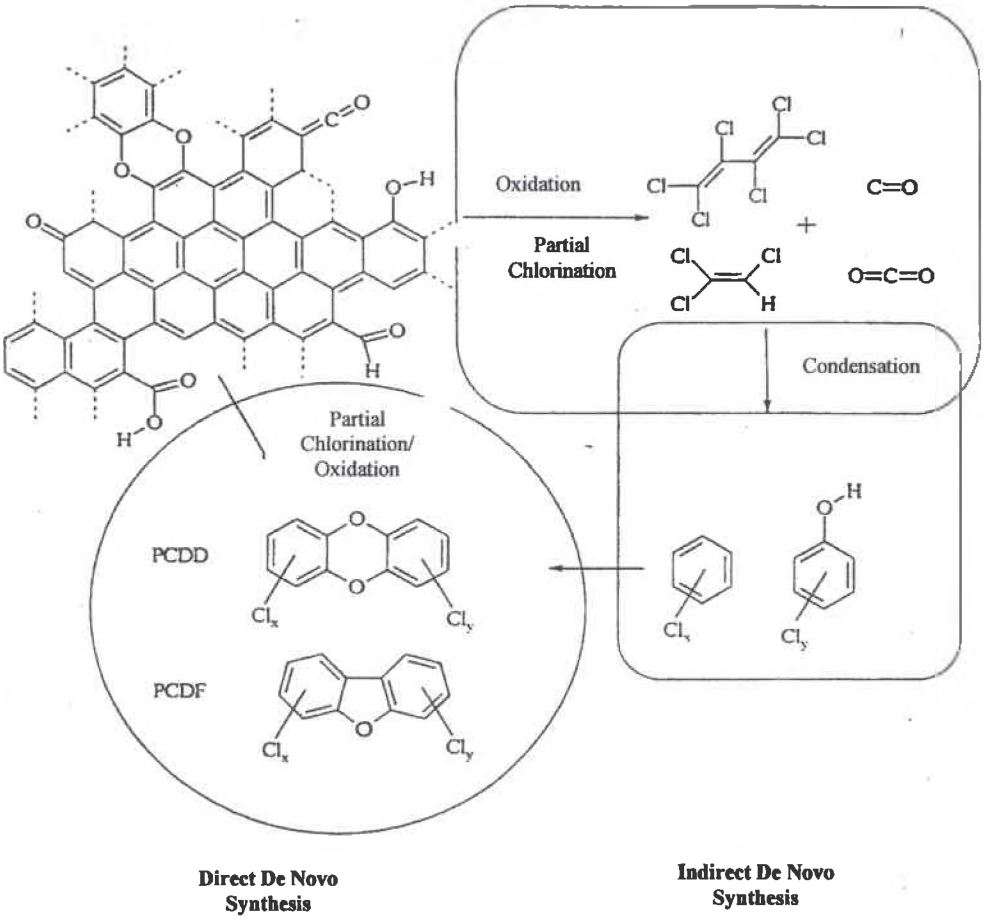


Figure 2.1. Formation of PCDD/F from *de novo* synthesis.

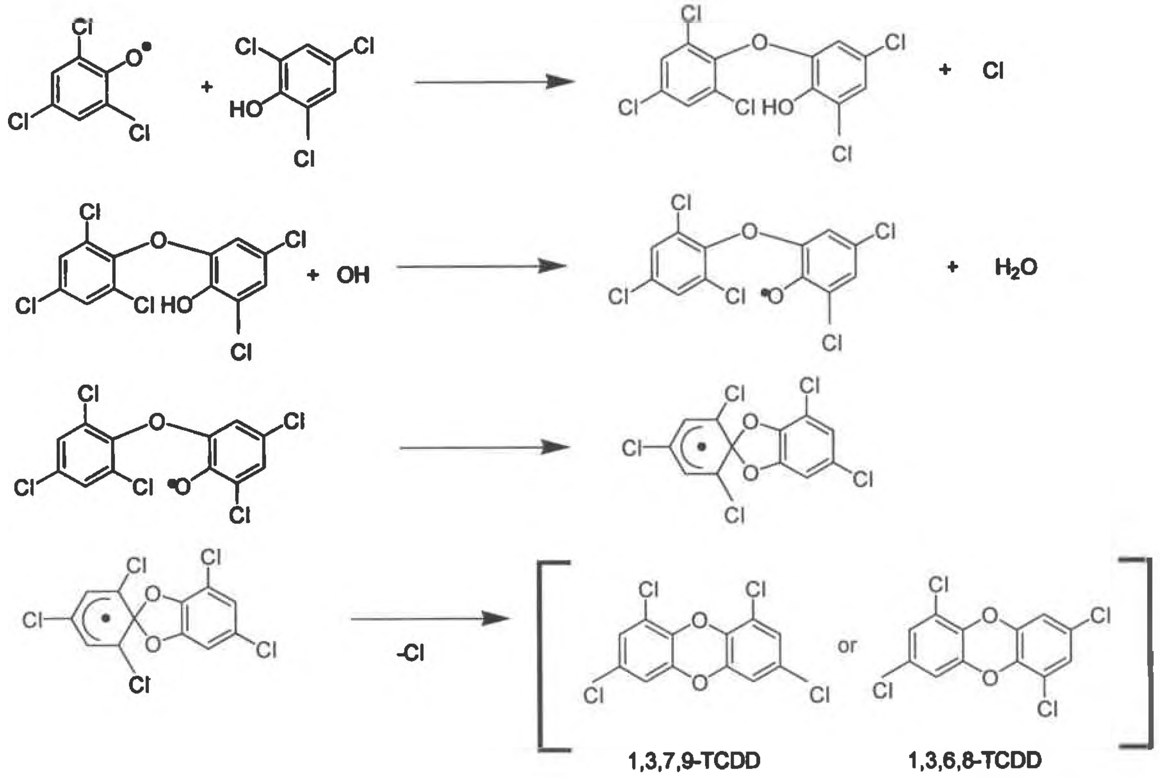


Figure 2.2. Formation of PCDD/F from chemically similar precursors.

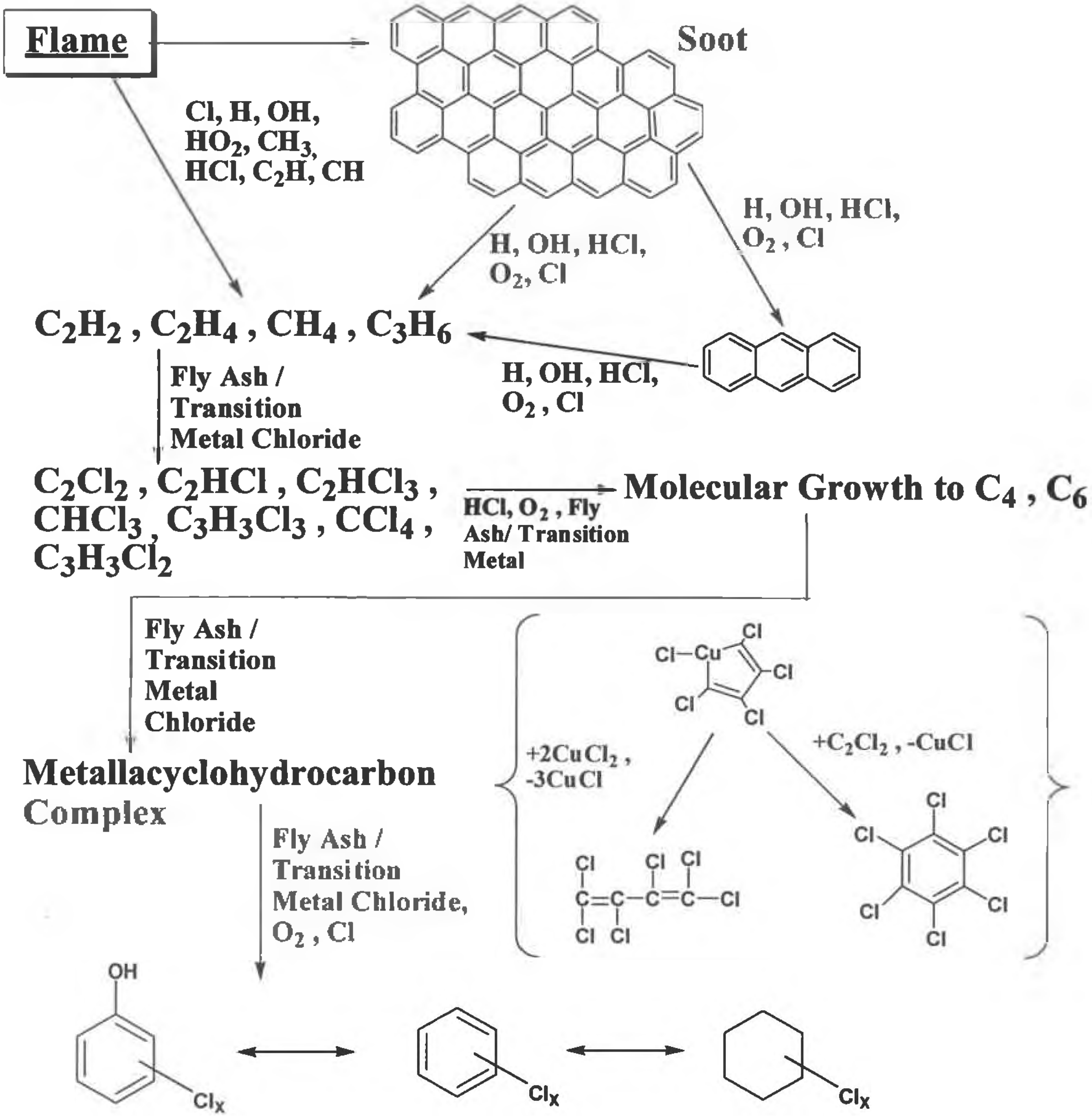


Figure 2.3. Global pathway to PCDD/F formation.

The objective of this study is to investigate the competitive chlorination of benzene and phenol, and to examine the oxidation of chlorobenzene and chlorophenol and the subsequent interactions of the phenoxy and phenyl radicals. While it is well documented that these compounds are the most direct precursors to PCDD/F formation and readily undergo condensation reactions to form dioxins, the nature of the competitive chlorination reactions and inter-conversion between the two is not well understood. Also, it is not known whether chlorobenzenes can form PCDD/F directly, or whether they must first pass through a phenol or phenoxy intermediate. A mechanistic and kinetic understanding of the surface-catalyzed and gas- phase formation of PCDD/F from precursors in conditions similar to those in MWI is quite useful in clarifying aspects of the global formation mechanism.

2.1 Heterogeneous Gas-Solid Experimental Objectives

The objective of the heterogeneous study is to examine the competitive chlorination and inter-conversion between known PCDD/F precursors (benzene and phenol) on surfaces present in significant quantities in the incinerator fly ash matrix. An elemental analysis of a typical fly ash sample is shown in Table 2.1. The chlorinating agent will consist of calcium, aluminum, iron, and potassium chlorides. The temperature region examined will be the low temperature region of the post combustion zone (300-500°C), where surface catalyzed reactions are known to occur. Typical residence times for gas-solid reactions (precursor adsorption, reaction, product desorption) are on the order of 200-400 milliseconds, and in these experiments residence times will be maintained at 25 ms to observe whether chlorination can occur in such a short time.

Table 2.1: Elemental Analysis of a Typical MWI Fly Ash Sample.

Al	**11%**
Ca	**9.3%**
K	**1.7%**
Fe	**12%**
Si	**22%**
S	**1.3%**
Ti	**0.69%**
Cu	**85 ppm**

2.2 Homogeneous Gas- Phase Experimental Objectives

The focus of these experiments is to investigate reactions of chlorinated phenols and benzenes and their respective phenoxy and phenyl radicals. The precursors examined are 2-chlorophenol (2-CP), 2-chloroanisole (2-CA), and monochlorobenzene (MCB). The corresponding phenoxy and phenyl radicals are shown in Figure 2.4.

Reaction conditions will simulate those in actual incinerators. Typical residence times of gases in the high temperature region of the post-combustion zone are around 2 seconds. Concentrations of chlorobenzenes and chlorophenols are observed to be less than 10 ppmv. Most previous work involves much higher precursor concentrations, and product distributions can vary substantially with concentration. Also, actual reaction conditions are very lean.

These experiments will illustrate the variation in reaction product distribution with respect to changing precursor concentration. Also, the importance of radical-radical and radical-molecule reactions in the PCDD/F formation mechanism will be investigated, and progress will be made toward the development of a fundamentally based PCDD/F formation model.

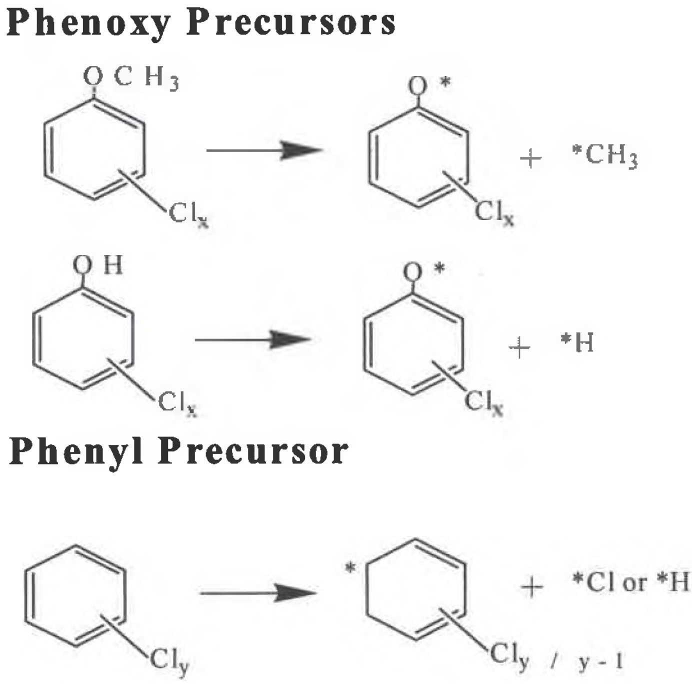


Figure 2.4. Phenoxy and phenyl radical precursors to PCDD/F formation.

CHAPTER III

EXPERIMENTAL

3.1 System

All experiments were performed using the System for Thermal Diagnostic Studies (STDS). The STDS is a high-temperature flow reactor coupled with an in-line gas chromatograph/ mass spectrometer (GC/ MS) system designed to simulate the reaction conditions in an incinerator post-flame zone. The setup is described in detail elsewhere [17]. Briefly, the STDS consists of four integrated units: 1) a control console for precise adjustment of temperature, pressure, residence time, and the respective gas flows; 2) a thermal reactor compartment containing a high temperature Lindberg furnace housed within a gas chromatograph (HP 5890) to allow precise sample introduction into and out of the quartz reactor; 3) a gas chromatographic oven (HP 5890) containing a capillary column (J & W Scientific DB-5, 30 m, 0.25 mm ID, 0.25 μm film thickness) for separation of organic reaction products; 4) a mass spectrometer (HP 5970B MSD) for product identification and quantification. A schematic of the STDS as modified for these experiments is shown in Figure 3.1.

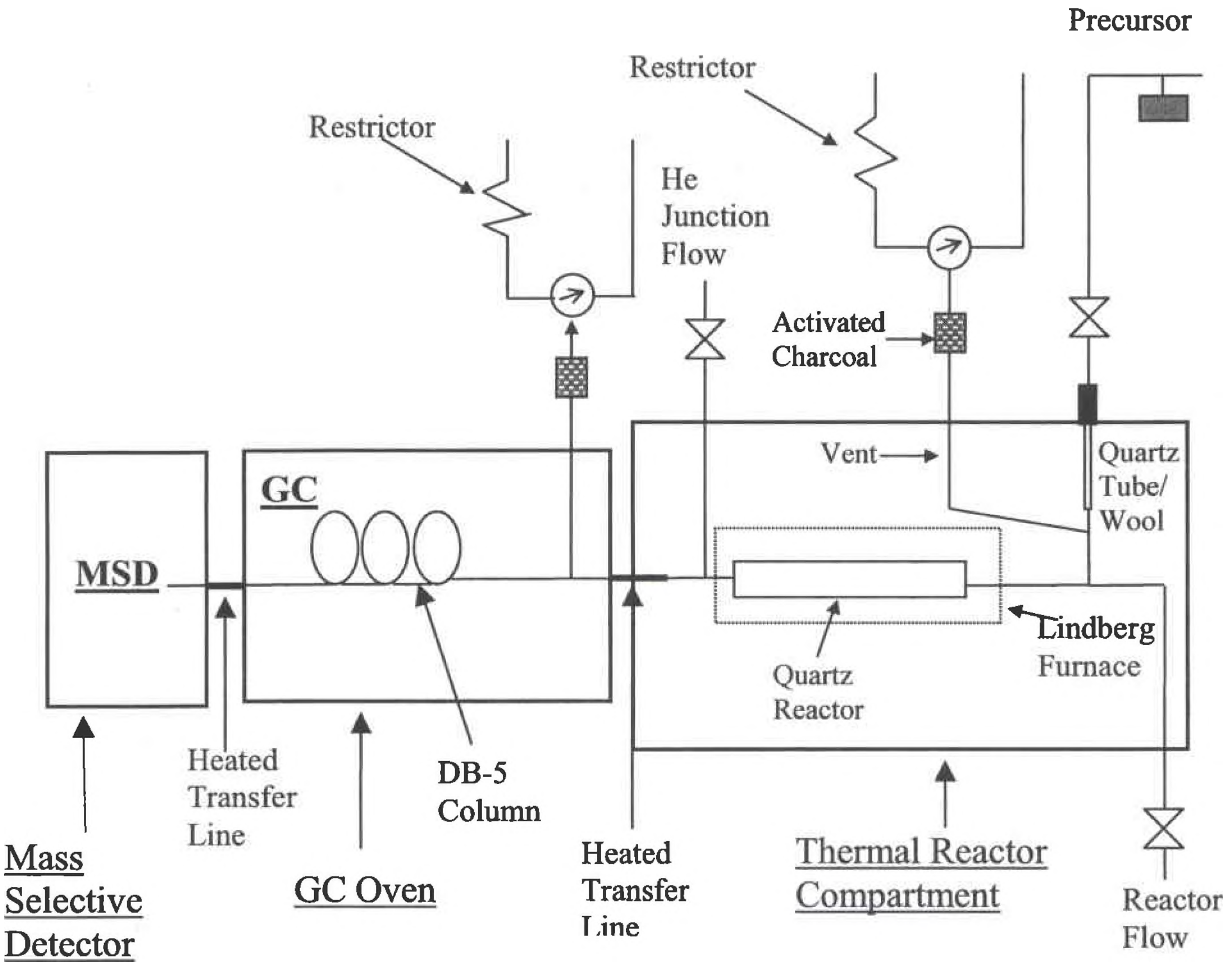


Figure 3.1. Schematic of the STDS As Modified for Heterogeneous Gas-Solid and Homogeneous Gas-Phase Studies.

3.2 Heterogeneous Gas-Solid Experiments

In the gas-solid experiments, the STDS was fitted with a 7.0 mm ID, 10 cm long quartz reactor. The chlorinating agent is loaded as a packed bed between quartz wool plugs inside the reactor. Forty mg of $CaCl_2$ and five mg each of $FeCl_3$, KCl, and $AlCl_3$ are used in each run, and the reaction gas used is 4%O_2 in helium at a flow rate of 30 to 40 ml/min (at RTP). A schematic of the reactor is shown in Figure 3.2.

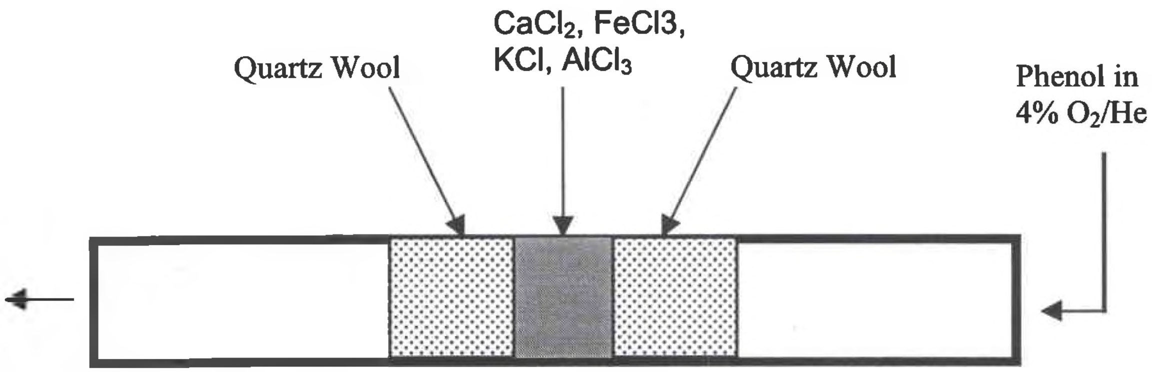


Figure 3.2. Schematic of the quartz packed bed reactor used in homogeneous gas-phase experiments.

The residence time of the reaction gas in the reactor is calculated by dividing the void volume of the chlorinating agent by the volumetric flow rate of the reaction gas, corrected for temperature and pressure:

$$t_r = \left(\frac{V_r}{F_o}\right)\left(\frac{T_o}{T_r}\right)\left(1+\frac{P_r}{P_o}\right) \qquad (3.2\text{-}1)$$

The subscript "$_o$" represents ambient conditions, and the subscript "$_r$" represents conditions in the reactor. V_r is the void volume of the packed bed (the void fraction of the chlorinating agent was measured by displacement to be 0.74 ± 0.11). F_o is the volumetric flow rate of the reaction gas measured at ambient temperature and pressure. The differential gauge pressure in the system (P_r) is measured by a digital transducer and converted from a millivolt reading to mm Hg. Residence times are maintained at 25 ± 9 milliseconds for a temperature range of 300 to 500 °C. At each reaction temperature, the flow rate F_o was calculated to maintain the 25 ms residence time.

The precursors examined were phenol and benzene. After temperatures and flows were set, 0.50 ± 0.07 mg of precursor were transferred into the injector, volatilized, and swept through the reactor. The reaction products and unreacted precursor were trapped at -60°C on a J&W Scientific DB-5 column (30 m, 0.25 mm ID, 0.25 μm film thickness). Products were analyzed using GC-MS with a temperature programming of -60°C (1 minute hold) to 300°C (10 minute hold) at a rate of 15°C/ minute.

Scanning mode was used to identify and quantitate reaction products from ranging from 15-350 AMU. Quantitation was performed using external standard calibration curves for the respective product. A few minor reaction products were quantitated using standard calibration for chemically similar compounds. A summary of the heterogeneous reaction conditions is found in Table 3.1.

Table 3.1: Summary of Heterogeneous Gas-Solid Reaction Parameters.

-Reactants:	Phenol; Benzene
- Chlorinating Agent:	40 mg $CaCl_2$ 5 mg $FeCl_3$, KCl, and $AlCl_3$
- Reaction Atmosphere:	4% O_2 in He; 30 – 40 ml/min
- Reactant Injection:	0.50 ± 0.07 mg
- Reaction Temperature:	300 – 500 °C
- Residence Time:	25 ± 9 milliseconds

3.3 Homogeneous Gas-Phase Experiments

In the gas-phase experiments, the STDS was fitted with a 1.0 cm ID, 27 cm^3 quartz reactor. The residence time distribution in the reactor simulates plug flow behavior. Previous studies in which the reactor diameter was varied from 0.1 to 1.2 cm have shown surface reactions of chlorinated hydrocarbons are insignificant for a reactor diameter $\geq$ 1.0 cm [8]. Also, the high temperature region was strictly confined to the wide bore section of the reactor to prohibit end surface effects. Therefore the system is completely homogeneous. A schematic of the reactor is shown in Figure 3.3.

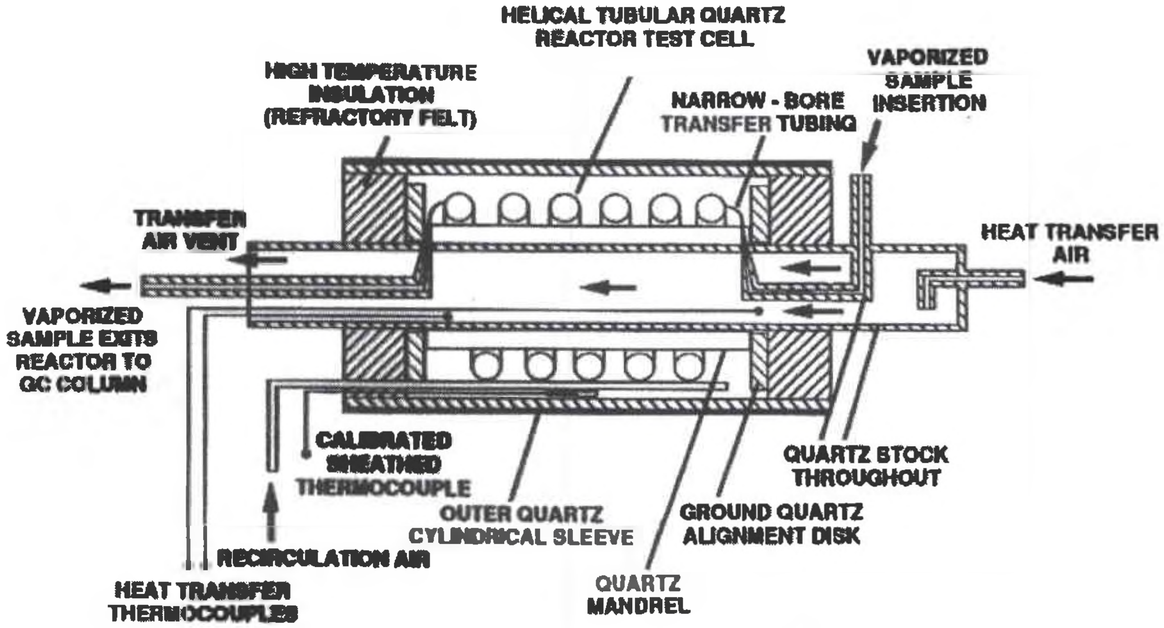


Figure 3.3. Schematic of the quartz plug-flow reactor used in homogeneous gas-phase reaction experiments.

The residence time of the reaction gas in the reactor is calculated by dividing the reactor volume by the volumetric flow rate of the reaction gas, corrected for temperature and pressure:

$$t_r = \left(\frac{V_r}{F_o}\right)\left(\frac{T_o}{T_r}\right)\left(1 + \frac{P_r}{P_o}\right) \qquad (3.3\text{-}1)$$

The subscript "$_o$" represents ambient conditions, and the subscript "$_r$" represents conditions in the reactor. V_r is the reactor volume and F_o is the volumetric flow rate of the reaction gas measured at ambient temperature and pressure. The differential gauge pressure in the system (P_r) is measured by a digital transducer and converted from a millivolt reading to mm Hg. Residence times are maintained at 2.0 ± 0.10 seconds for a temperature range of 400 to 800 °C. At each reaction temperature, the flow rate F_o was adjusted to maintain the 2 second residence time. Reactions were conducted in an atmosphere of 4% oxygen in helium.

The precursors examined were 2-chlorophenol (2-CP), 2-chloroanisole (2-CA), and monochlorobenzene (MCB). To achieve low precursor concentration but stay within detection limits, the gas-phase precursor concentration in the reaction gas was maintained at 4 ± 1 PPM (2.1×10^4 $\mu g/m^3$ at RTP). A gas-phase sample of precursor in helium was prepared in a 0.52 liter sample bulb for each run. During the runs, the sample was injected into the reactor at a constant rate using a syringe pump (Sage Instruments Model 341A). For each run, a syringe pump flow rate setting was selected and the required concentration of precursor in the sample bulb was calculated to maintain a precursor concentration in the reaction gas of 4 PPM. The molar equivalence ratio was calculated using the equation:

$$\phi = \left(\frac{n_{PRECURSOR}}{n_{O_2}} \right)_{ACTUAL} \Bigg/ \left(\frac{n_{PRECURSOR}}{n_{O_2}} \right)_{STOICHIOMETRIC} \qquad (3.3\text{-}2)$$

The equivalence ratios for 2-CP, 2-CA, and MCB were 6.76 x 10^{-4}, 8.26 x 10^{-4}, and 7.25 x 10^{-4}, respectively (fuel lean conditions).

The reaction products and unreacted precursor were trapped with a composite adsorptive trap consisting of 0.12 g of TENAX-TA® and 0.24 g of CARBOTRAP®. The trap is shown in Figure 3.4. After each run, the trap was desorbed at 300°C for 20 minutes, and the reaction products were trapped at 30°C on a J&W Scientific DB-5 column (30 m, 0.25 mm ID, 0.25 μm film thickness). Products were analyzed using GC-MS with a temperature programming of 30°C (1 minute hold) to 300°C (10 minute hold) at a rate of 15°C/ minute.

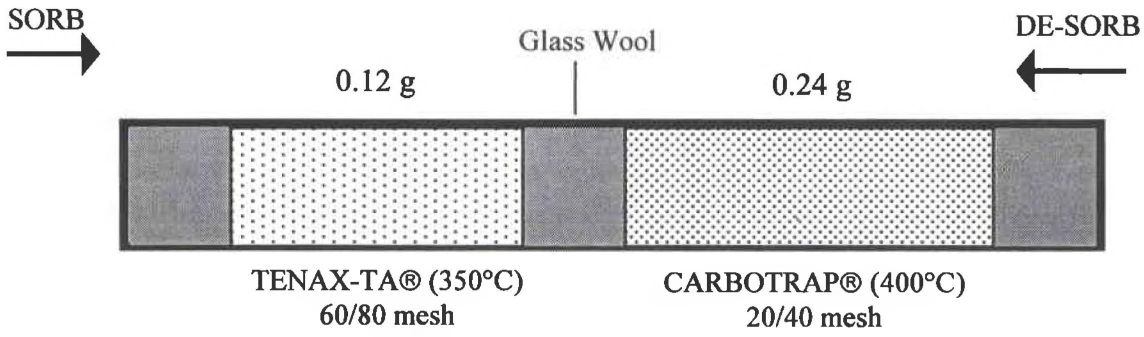


Figure 3.4. Composite adsorptive trap used in homogeneous gas-phase experiments.

Selected ion monitoring (SIM) was used for identification and quantitation of reaction products. For PCDD/F analysis, the molecular weight (M) and molecular weight + 2 (M+2) ions along with one other prominent ion were monitored. For other products, the molecular weight ion and two other prominent ions in the compound's spectrum were monitored.

Quantitation was performed using external standard calibration curves for the respective product. A few minor reaction products were quantitated using standard calibration for chemically similar compounds. The calibration curve used to quantitate dioxins is shown in Figure 3.5.

A summary of the homogeneous reaction conditions is found in Table 3.2.

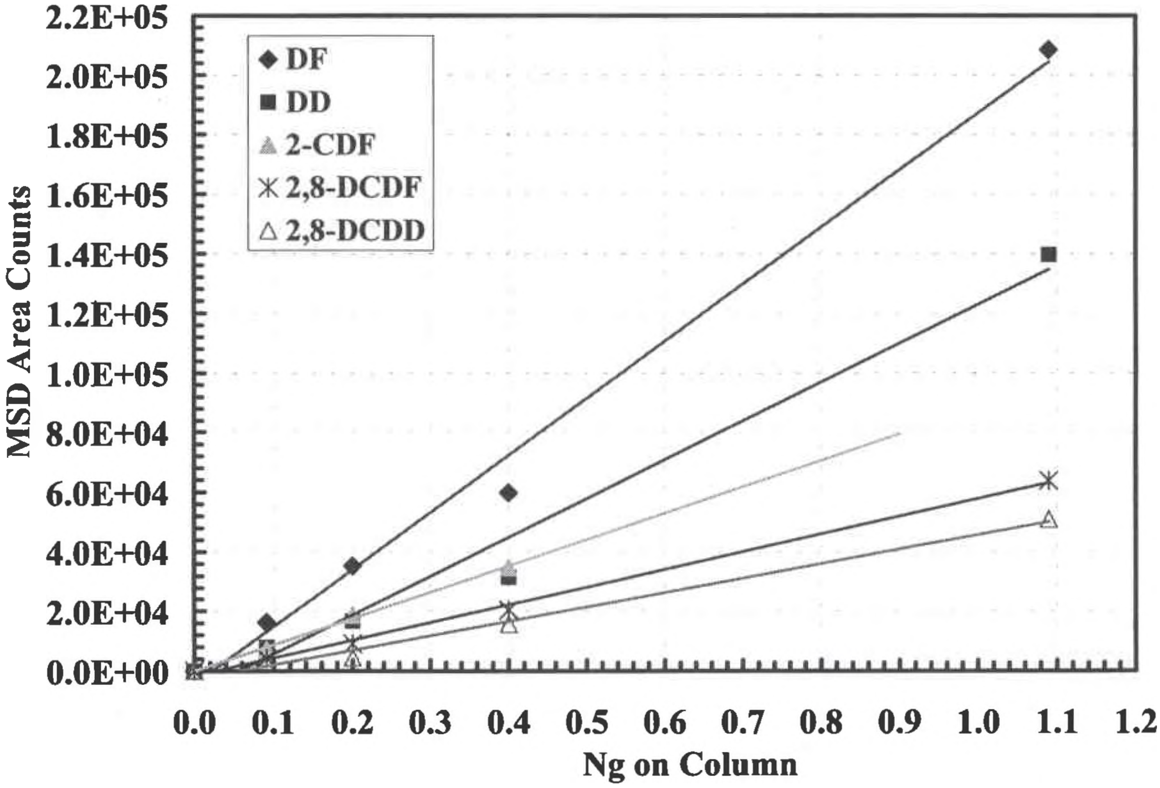


Figure 3.5. External standard calibration curves for quantitation of PCDD/F products.

Table 3.2: Summary of Homogeneous Gas-Phase Reaction Parameters.

-Reactants:	2-Chlorophenol (2-CP); 2-Chloroanisole (2-CA); Monochlorobenzene (MCB)
- Reaction Atmosphere:	4% Oxygen in Helium
- Reactant Concentration:	4 ± 1 PPM
- Reaction Temperature:	400 – 800 °C
- Residence Time:	2.00 ± 0.10 sec
- Molar Equivalence Ratio:	2-CP: 6.76×10^{-4} 2-CA: 8.26×10^{4} MCB: 7.25×10^{4}
- Reaction Time:	60 - 80 min

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Heterogeneous Gas-Solid Results

The chlorination of phenol and benzene has been studied at temperatures ranging from 300-500°C. Residence times are maintained at 25 ± 9 milliseconds. A 30 to 40 ml/min flow (at RTP) of 4% oxygen in helium containing 0.50 ± 0.07 mg of precursor is passed over a packed bed consisting of $CaCl_2$, KCl, $FeCl_3$, and $AlCl_3$. Similar reaction products are observed from each precursor. Major aliphatic products are chloroform ($CHCl_3$), carbon tetrachloride (CCl_4), chloroethylene (C_2H_3Cl), dichloroethylene ($C_2H_2Cl_2$), trichloroethylene (C_2HCl_3), and tetrachloroethylene (C_2Cl_4). Major aromatic products are chlorobenzenes and chlorophenols. A full complement (mono- through hexachloro- for benzene and mono- through pentachloro- for phenol) of chlorinated phenols and benzenes are observed from phenol reactions, and a full complement of chlorobenzenes and a few chlorophenol isomers are observed from benzene reactions.

At 300°C, yields of aliphatic products from benzene are much higher than those from phenol, but at 500°C, yields of aliphatics from phenol become higher. Similarly, yields of chlorinated benzenes are highest from benzene at 300°C, but at 400 and 500°C, yields from phenol become higher. Yields of chlorinated phenol products from the phenol precursor are always higher than those from benzene, but significant amounts of mono, di, and tetrachlorophenols are produced from benzene. Yields of chlorinated phenols from both precursors are maximum at 300°C. At higher temperatures, phenol begins to form decomposition and molecular growth products. Non-chlorinated dibenzo-p-dioxin and dibenzofuran are observed from the phenol precursor, but no chlorinated PCDD/F products are observed. It is probable that they were formed, but stayed adsorbed to the surface of the catalyst mixture, which was not extracted. Major product yields from chlorination of phenol and benzene (shown as mole percent yields based on precursor input) are shown on Figure 4.1. Raw data is shown in Appendix 1.

4.1.1 Heterogeneous Gas-Solid Conclusions

In conclusion, chlorination was found to occur readily at very short residence times (25 ms). Also, benzene is more likely to produce aliphatic products at lower temperatures and has a maximum conversion to chlorinated products at 300°C. Phenol produces more chlorinated aromatic products and shows a maximum conversion at higher temperatures (400-500°). This is because the phenoxy precursor has a much higher affinity for adsorption than does the phenyl precursor, and so phenols can adsorb at much higher temperatures than can benzene. There is clearly significant inter-conversion between chlorinated benzenes and chlorinated phenols.

It is known that benzene and phenol are very important in PCDD/F formation, and it has been demonstrated in these experiments that they are quite easily chlorinated. It is useful now to study the reactions of chlorinated benzenes and phenols and their radicals in relation to PCDD/F formation. This will be done purely in the gas-phase, so as to bypass the added complexities associated with catalytic surface effects.

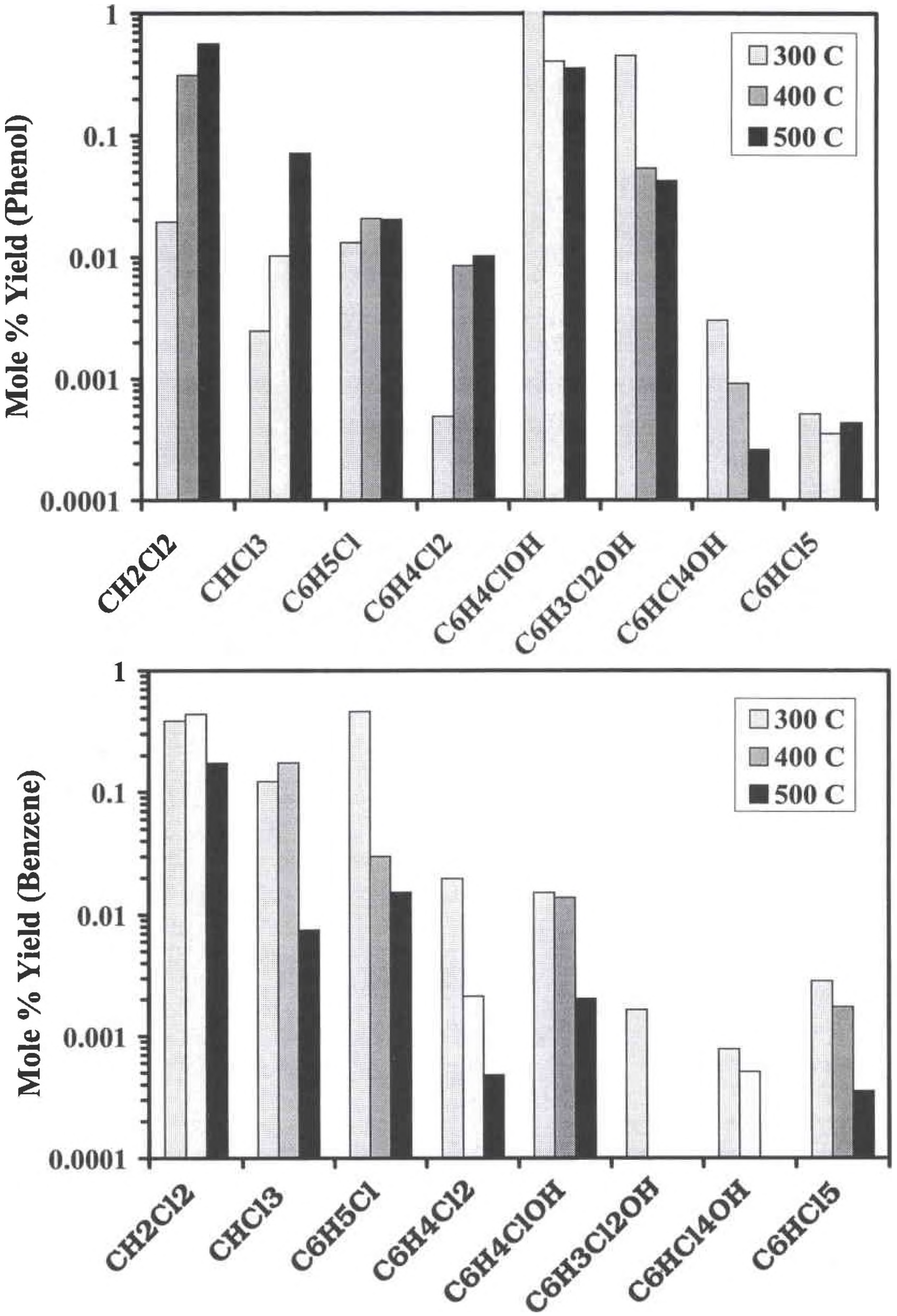


Figure 4.1. Major product yields from *phenol* (top) and *benzene* (bottom) on 40 mg $CaCl_2$; 5 mg KCl, $AlCl_3$, $FeCl_3$. t_r = 25 ms in 4% O_2/He.

4.2 Homogeneous Gas-Phase Results

In this work, the role of phenoxy and phenyl radicals is investigated by studying the slow oxidation of 2-Chlorophenol, 2-Chloroanisole, and monochlorobenzene at a gas-phase concentration of 4 PPM (~2.1 x 10^4 μg/m^3) over a temperature range of 400 to 800°C. Residence times are maintained at 2.0 ± 0.10 seconds. Major products in these experiments are Phenol (PH), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 3-phenyl-2-propenal, 1-indanone, 1,3-isobenzofurandione, 3-phenyl-2-propenoyl chloride, diphenyl ether (DPE), and naphthalene (NA). Major PCDD/F reaction products are dibenzofuran (DF), dibenzo-p-dioxin (DD), 4-chlorodibenzofuran (4-CDF), 1-chlorodibenzo-p-dioxin (1-CDD), 4,6-dichlorodibenzofuran (4,6-DCDF), and 1,9-dichlorodibenzo-p-dioxin (1,9-DCDD). Reaction products and their structures are listed in Table 4.1, and a comparison of the product yields (mass percent yields based on precursor input) from 2-CP, 2-CA, and MCB at 600°C is shown in Figure 4.12.

4.2.1 2-Chlorophenol Experiments

The product profiles of non-PCDD/F products for 2-CP oxidation experiments are shown in Figure 4.2. The major non-PCDD/F product is 3-phenyl-2-propenal, with a mass percent yield of 0.13% at 650°C. Other products are formed in yields between 0.01-0.10%. Maximum yields of non-PCDD/F products occurred from 650-700°C. The PCDD/F product profiles are shown in Figure 4.3. The major PCDD/F product is 1-CDD, with a maximum mass percent yield of 0.03% at 650°C. Other PCDD/F products are produced in yields of 0.001-0.007%, with the maximum yield of PCDD/F products occurring from 600-650°C. The gas-phase 2-chlorophenol is observed to be fairly stable, with slight decomposition beginning at 500°C, but rapid decomposition only after about 650°C.

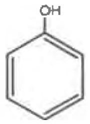
PCDD/F products are formed as a result of radical-molecule and radical-radical reactions between the 2-chlorophenoxy radical and the 2-chlorophenol molecule. Thermochemical and kinetic analysis has previously concluded that the molecule-molecule reaction is infeasible in 2-chlorophenol under the reaction conditions in this study [13]. In the radical-molecule reaction (see Figure 4.4), non-chlorinated dibenzo-p-dioxin (DD) and dibenzofuran (DF) are formed as major products along with 1-chlorodibenzo-p-dioxin (1-CDD) and 4-chlorodibenzofuran (4-CDF) as minor products. In dioxin formation, the initial step is the displacement of the molecule's chlorine by the phenoxy radical. The resulting compound can then either abstract HCl to directly form DD or can lose a hydrogen by OH• abstraction to form a *phenoxy* ether intermediate (*I1* in Figure 4.4). The intermediate then undergoes Smile's rearrangement to form either DD through intra-ring elimination of the second chlorine atom or 1-CDD through intra-ring elimination of hydrogen. Alternatively, in dibenzofuran formation the initial step is instead the displacement of OH• by the phenoxy radical. The resulting compound can then either abstract HCl to directly form 4-CDF or lose hydrogen with the help of OH• to form a *phenyl* ether intermediate (*I2* in Figure 4.4). The intermediate then undergoes Smile's rearrangement to form either DF through intra-ring elimination of the second chlorine atom or 4-CDF through intra-ring elimination of hydrogen. Smile's rearrangement is a well-documented occurrence in these types of reactions [18].

Phenoxy or chlorophenoxy radicals exist in equilibrium with their "keto" forms. The keto form is the more stable form of the radical. In the radical-radical reaction to PCDD, keto- and phenoxy react to form an ether adduct. This is then followed by hydrogen tautomerism. The resulting compound (*I3* in Figure 4.5) can then either abstract HCl to directly form 1-CDD or lose a hydrogen atom by OH• abstraction to form a chlorophenyl-chlorophenoxy ether intermediate. This intermediate then undergoes Smile's rearrangement to form either 1-CDD through intra-ring elimination of the second chlorine atom or 1,9-DCDD through intra-ring elimination of hydrogen. The intermediate *I3* (dichloro-diphenyl-hydroxy-diphenyl ether) has been consistently observed in the homogeneous reaction experiments from 2-chlorophenol.

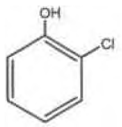
In the radical-radical reaction to PCDF (see Figure 4.6), chlorophenoxy radicals move into keto formation and then react in slightly different arrangements to form either a mono-chlorinated or di-chlorinated biphenoxy intermediate (with two ketone groups). This intermediate then undergoes hydrogen tautomerism to convert the ketone groups into hydroxyl groups. This molecule can then eliminate a hydroxyl radical or water to form 4-chlorodibenzodioxin (major) or 4,6-dichlorodibenzofuran (minor). The monochloro-biphenoxy intermediate has also been consistently observed in the homogeneous reaction experiments from 2-chlorophenol.

Table 4.1: Major reaction products and their chemical structures.

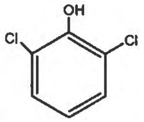
Phenol (PH)



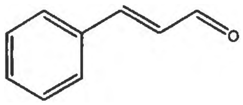
2-Chlorophenol (2-CP)



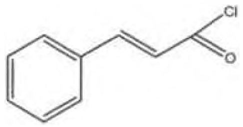
2,6-Dichlorophenol (2,6-DCP)



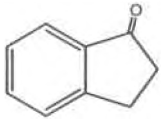
3-Phenyl-2-propenal (3-Ph-2-prop)



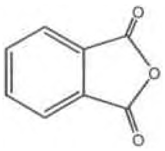
3-Phenyl-2-propenoyl chloride



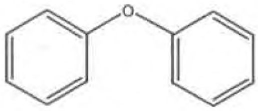
1-Indanone (1-Ind)



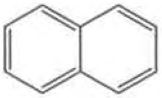
1,3-Isobenzofurandione (1,3-IsoBF)



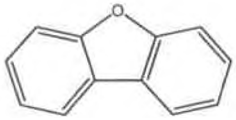
Diphenyl ether (DPE)



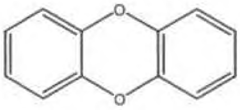
Naphthalene (NA)



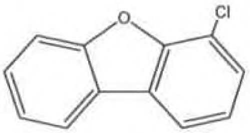
Dibenzofuran (DF)



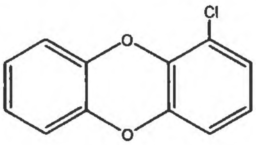
Dibenzo-p-dioxin (DD)



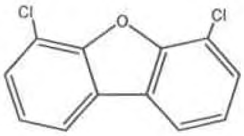
4-Chlorodibenzofuran (1-CDF)



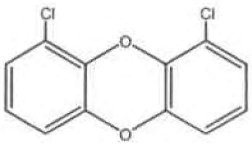
1-Chlorodibenzo-p-dioxin (1-CDD)



4,6-Dichlorodibenzofuran (1,9-DCDF)



1,9-Dichlorodibenzo-p-dioxin (1,9-DCDD)



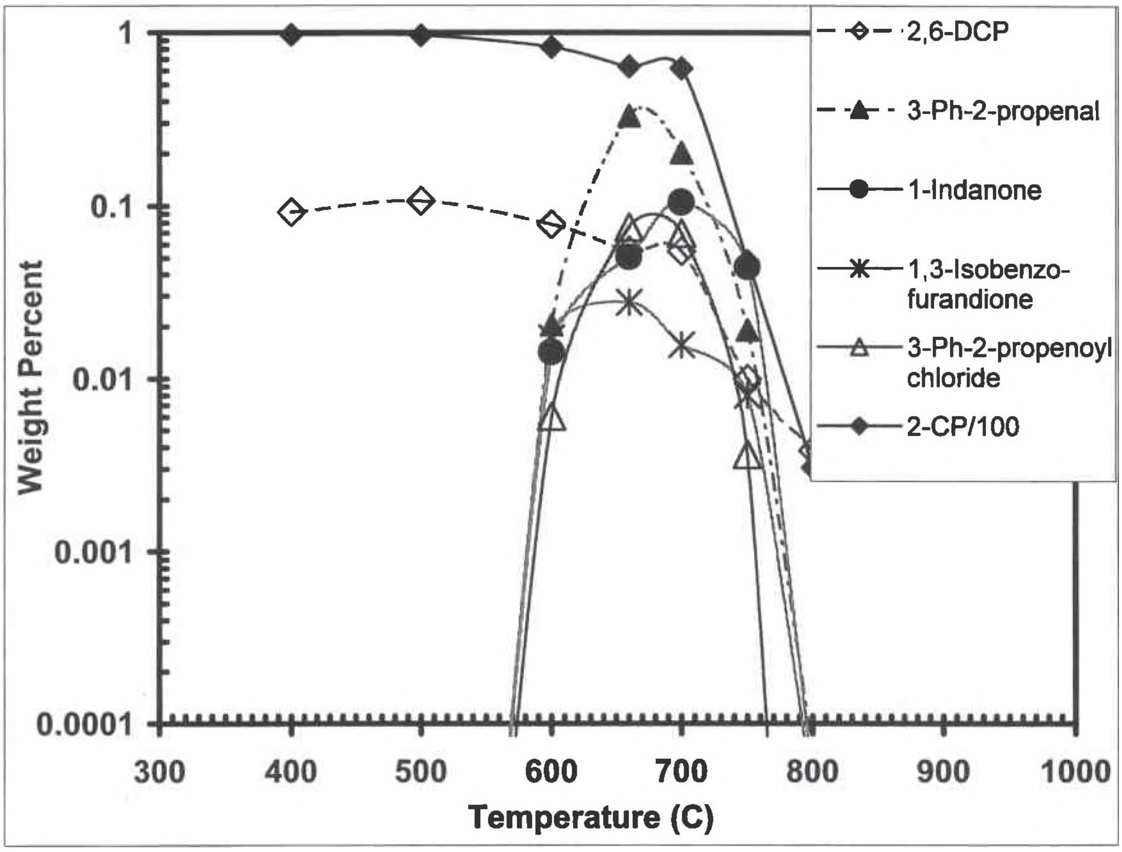


Figure 4.2. Thermal oxidation profiles for 2-chlorophenol *non*-PCDD/F products and product yields in mass percent. $[2\text{-CP}]_0 = 2.1 \times 10^4$ μg/m^3 (RTP), $t_r = 2.0$ sec in 4% O_2 / He.

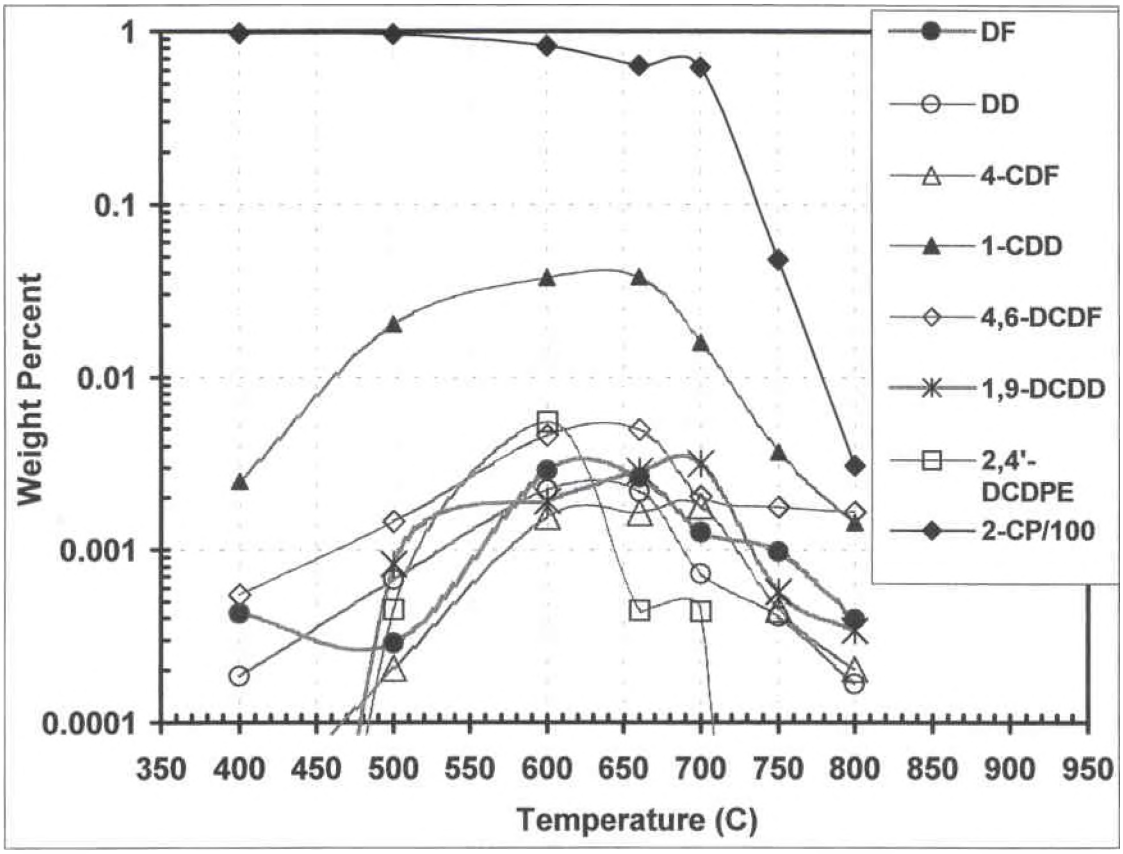


Figure 4.3. Thermal oxidation profiles for 2-chlorophenol and PCDD/F product yields in mass percent. $[2\text{-CP}]_0 = 2.1 \times 10^4$ μg/m^3 (RTP), $t_r = 2.0$ sec in 4% O_2 / He.

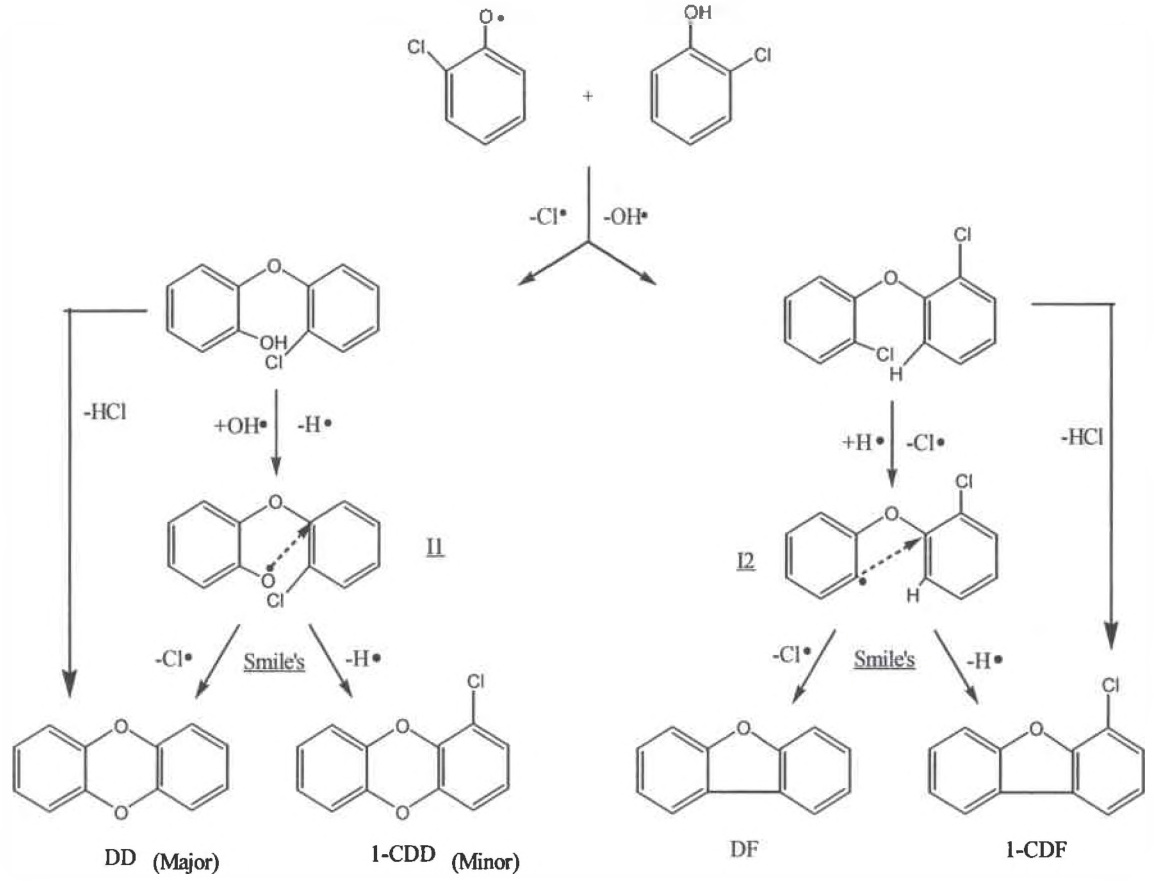


Figure 4.4. Radical-molecule pathway to PCDD/F formation from oxidation of 2-chlorophenol.

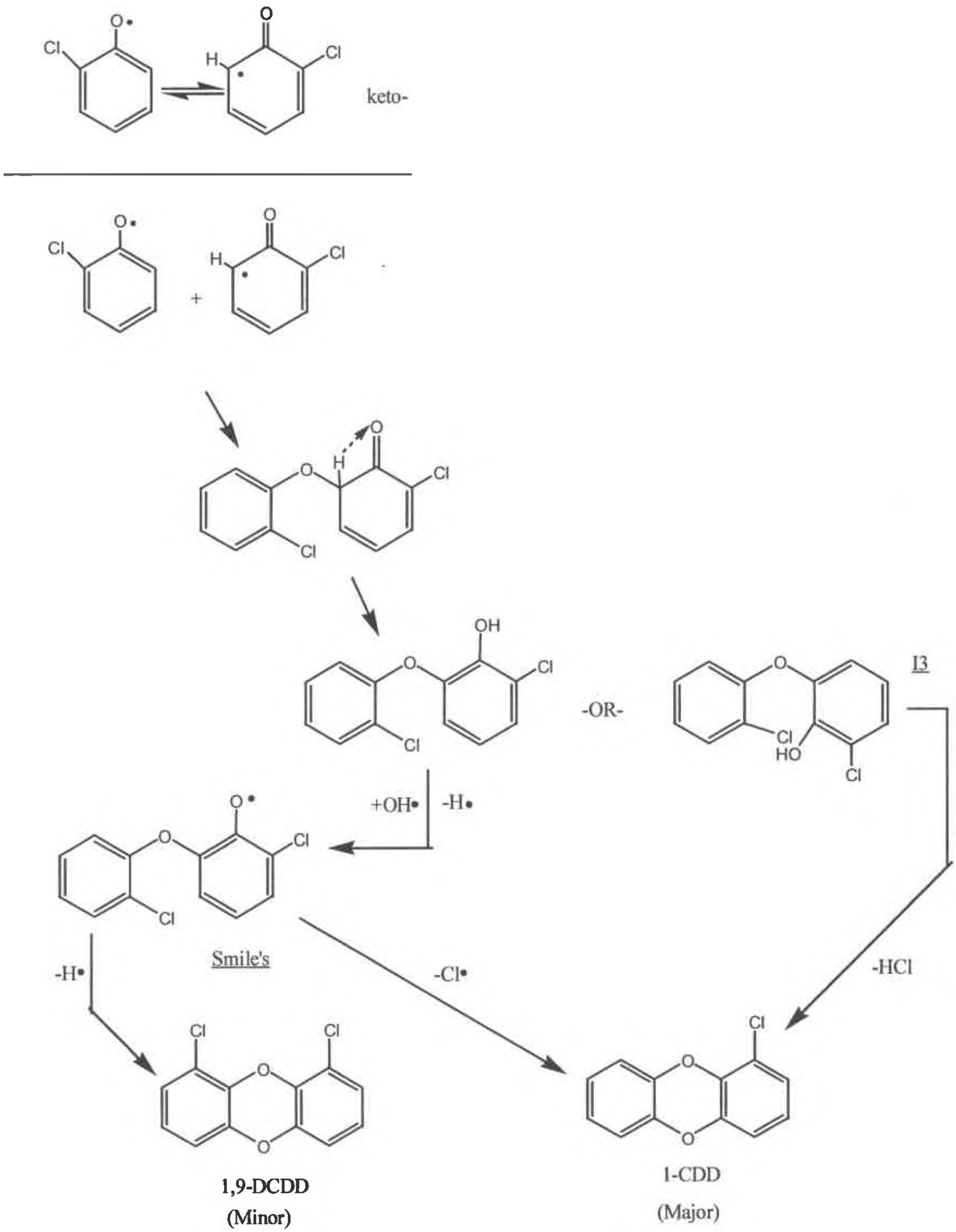
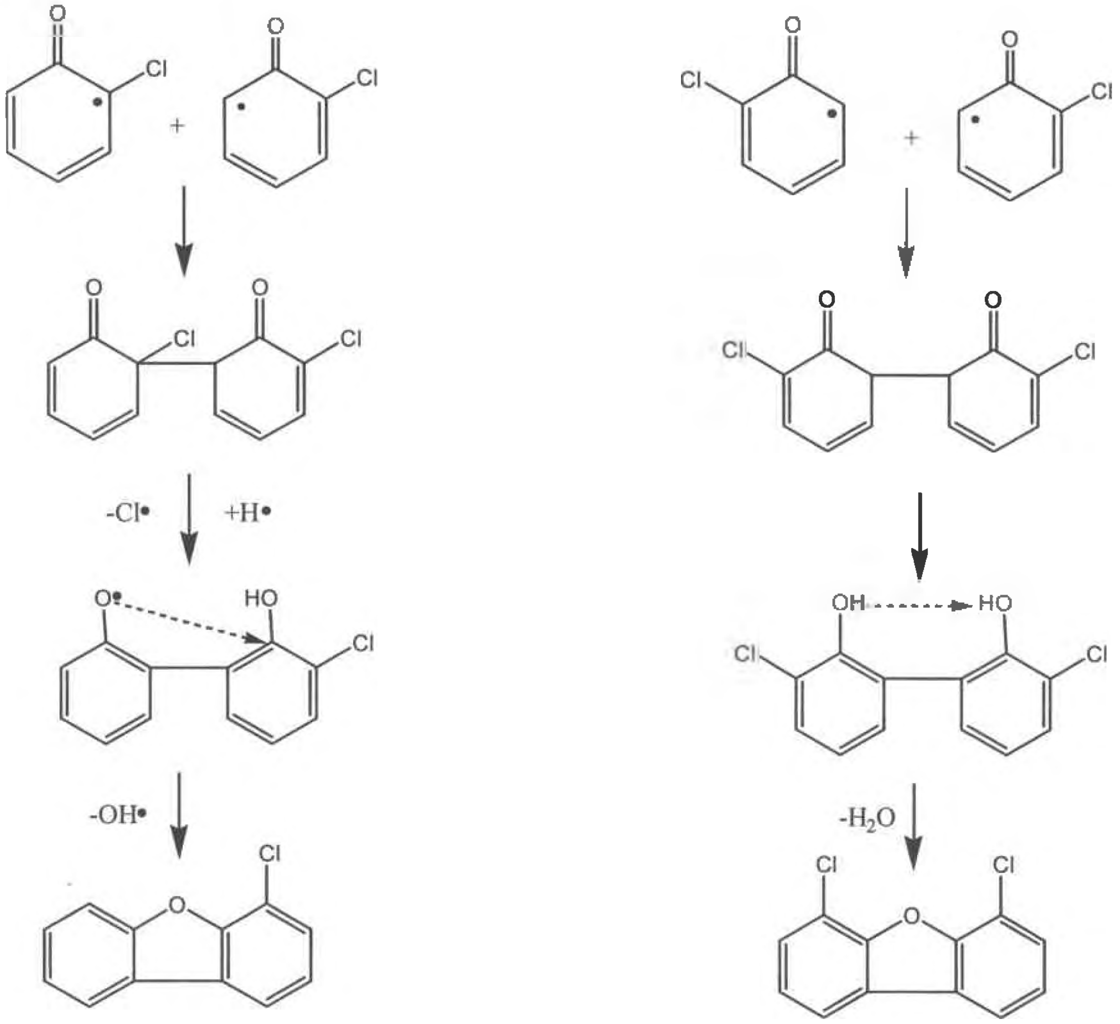


Figure 4.5. Radical-radical pathway to PCDD formation from oxidation of 2-chlorophenol.



1-CDF (Minor)

(Major) 1,9-DCDF

Figure 4.6. Radical-radical pathway to PCDF formation from oxidation of 2-chlorophenol.

4.2.2 2-Chloroanisole Experiments

The product profiles of non-PCDD/F products for 2-chloranisole oxidation are shown in Figure 4.7. Similar non-PCDD/F products are observed as in the 2-chlorophenol experiments, but lower mass percent yields were observed from 2-CA than from 2-CP. Yields from 2-CA range from 0.001% to 0.04% at 600°C. The major non-PCDD/F product from 2-CP is 3-phenyl-2-propenal, but from 2-CA the major oxidation product is 1-indanone, with a maximum yield of 0.04% at 600°C. Maximum yields of non-PCDD/F products from 2-CA also occur around 600°C, but formation begins at lower temperatures (500°C) from 2-CA than from 2-CP.

The PCDD/F product profiles are shown in Figure 4.8. Similar PCDD/F products were observed as in the 2-CP experiments, but yields were lower from 2-CA than from 2-CP. The major PCDD/F product from 2-CA was 4,6-dichlorodibenzofuran, with a maximum mass percent yield of 0.002% at 700°C (the major product from 2-CP was 1-CDD at 0.03% at 650°C). Other PCDD/F products are produced in yields of 0.0002-0.001%, with the maximum yield of PCDD/F products occurring from 500-700°C. The gas-phase 2-chloroanisole is observed to be less stable than 2-chlorophenol, with decomposition beginning at 500°C (similar to 2-CP), but with very rapid decomposition thereafter.

The O-CH_3 bond strength of 2-chloroanisole (~96.5 kcal/mol as estimated by group additivity) is less than the O-H bond strength of 2-chlorophenol (~104.1 kcal/mol as estimated by group additivity), and phenoxy radicals and methyl radicals are generated at lower temperatures from 2-CA than from 2-CP, causing rapid decomposition of 2-CA compared to 2-CP. This is why product formation from 2-CA occurs over a broader temperature range than from 2-CP. The methyl radicals create a radical pool that is not present with chlorophenol, in which many reactions take place such as:

$$CH_3\bullet + CH_3\bullet \leftrightarrow C_2H_6 \quad ; \quad C_2H_6 \leftrightarrow C_2H_5\bullet + H\bullet \text{ , etc.}$$

This radical pool creates a very reactive system, in which it is somewhat more difficult to form large molecular growth molecules such as PCDD/F. However, it is observed that dioxin formation is reduced more than furan formation when comparing yields from 2-CA with 2-CP (the major PCDD/F product from 2-CA is 4,6-DCDF, where it was 1-CDD in the 2-CP experiments, and the furans in general become dominant in 2-CA oxidation). This is because dioxin formation is very reliant upon the phenoxy-"keto" radical equilibrium, whereas furan formation involves only the more stable "keto" form of the radical. The radical pool introduced with the methyl group of 2-chloroanisole competes for unstable radicals, quickly forming compounds like methane, methanol, ethane, ethanol, etc. before dioxin formation can take place. Hence, yields of dioxin products decrease markedly with the introduction of the methyl group, while yields of 4,6-DCDF decreased, but to a lesser extent.

This is consistent with results from previous work in which oxidation experiments were conducted with 2,4,6-trichlorophenol (2,4,6-TCP) alone and with hexane. The introduction of the extra radicals produced from the decomposition of hexane caused a decrease in the yields of PCDD products, while PCDF yields did not show the same effect, and were even observed to increase [19].

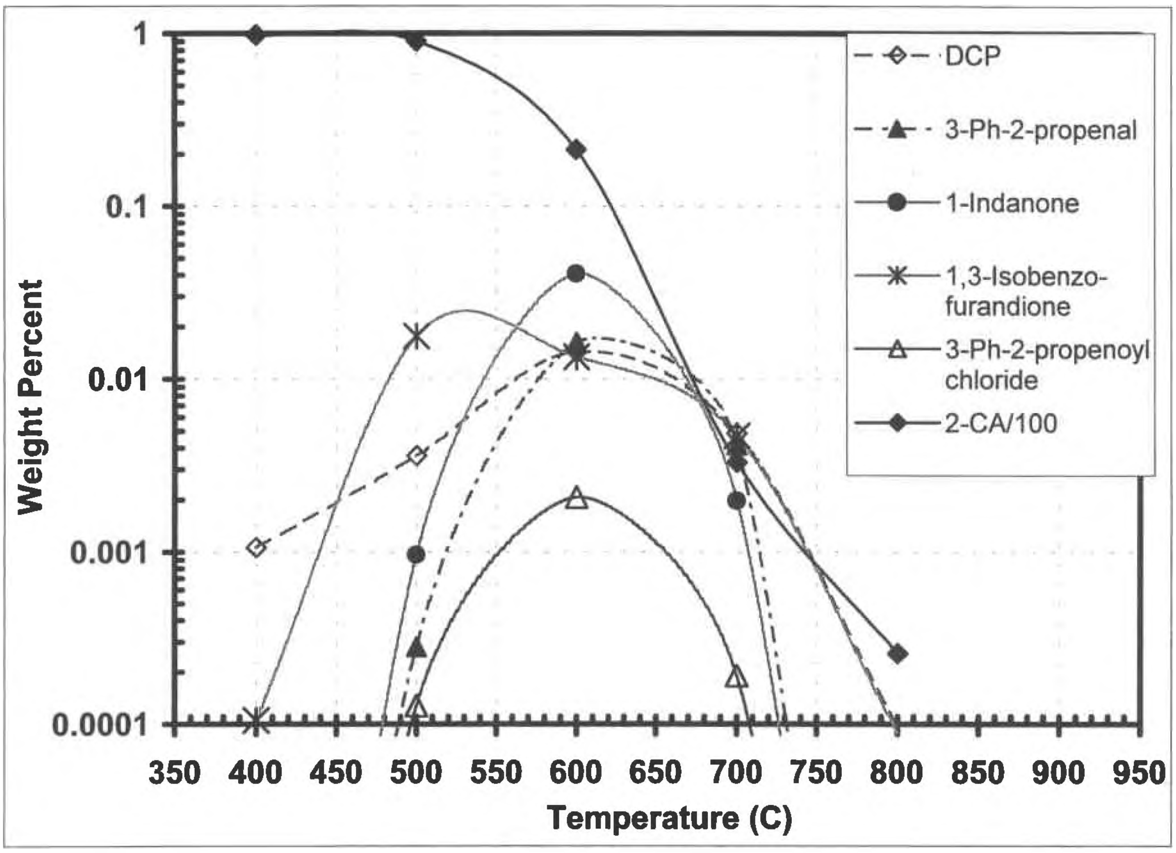


Figure 4.7 Thermal oxidation profiles for 2-chloroanisole and *non*-PCDD/F product yields in mass percent. $[2\text{-CA}]_0 = 2.1 \times 10^4$ μg/m^3 (RTP), $t_r = 2.0$ sec in 4% O_2 / He.

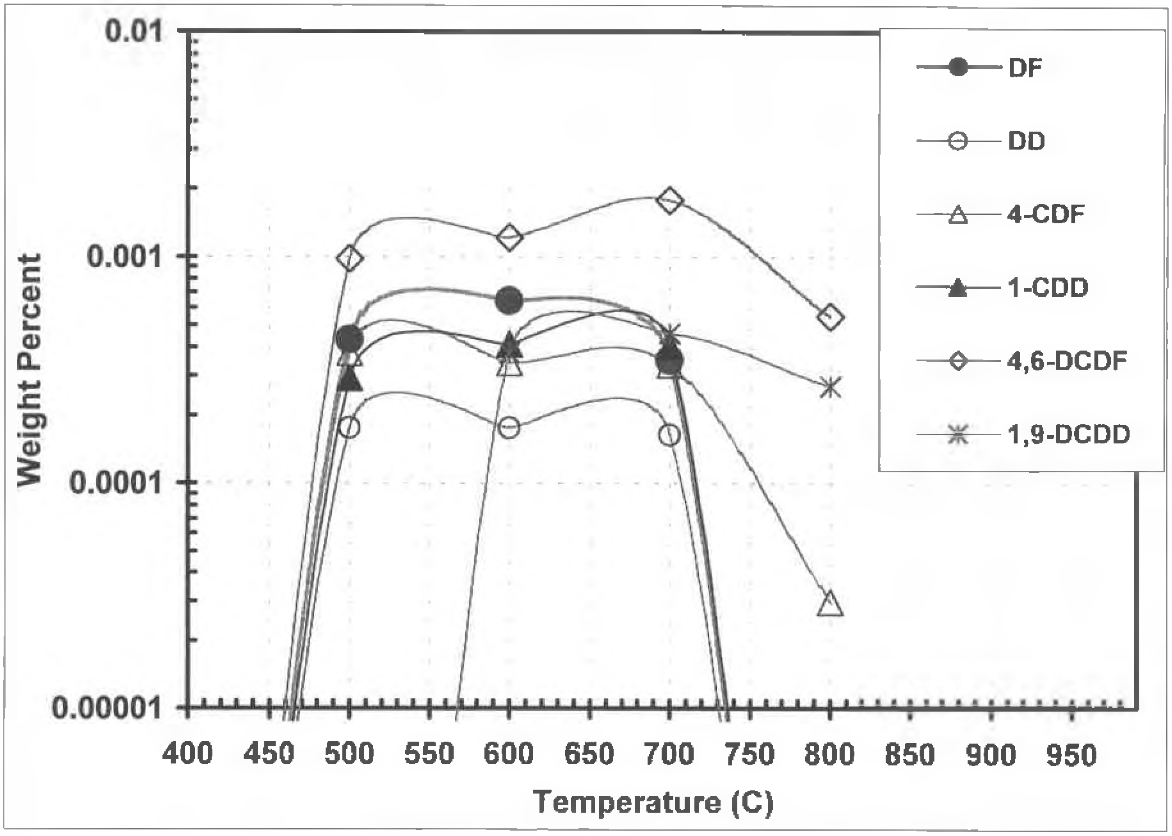


Figure 4.8. Thermal oxidation profiles for 2-chloroanisole and PCDD/F product yields in mass percent. $[2\text{-CP}]_0 = 2.1 \times 10^4$ μg/m^3 (RTP), $t_r = 2.0$ sec in 4% O_2 / He.

4.2.3 Monochlorobenzene Experiments

The product profiles of non-PCDD/F products from monochlorobenzene (MCB) oxidation are shown in Figure 4.9. The major non-PCDD/F products are phenol, 2-CP, and 4-CP, which are formed at maximum yields of 0.03-0.3% at temperatures of 600 to 700°C. Diphenyl ether and naphthalene are also produced, with maximum yields of 0.01-0.02% at temperatures of 600 to 700°C. The major non-PCDD/F products seen in the 2-CP and 2-CA runs are not observed in MCB experiments.

The PCDD/F product profiles are shown in Figure 4.10. The only products observed were DF, 4-CDF, 4,6-DCDF, and DD, with yields much lower than from 2-CA or 2-CP oxidation. The major PCDD/F product is DF, with a maximum mass percent yield of 0.002% at 700°C. Other PCDD/F products (4,6-DCDF, 6-CDF, and DD) are produced in yields of 0.0002-0.001%, with the maximum yield of PCDD/F products occurring around 700°C. The gas-phase monochlorobenzene is observed to be fairly stable, with only slight decomposition up to 700°C, and rapid decomposition at higher temperatures. The raw data collected for the 2-CP, 2-CA, and MCB experiments can be seen in Appendix 2. A comparison of the product yields from 2-CP, 2-CA, and MCB at 600°C is shown in Figure 4.12.

The chlorobenzene molecule can form either the phenyl radical or the phenoxy radical. Diphenyl ether is formed by the combination of a phenoxy and a phenyl radical, and naphthalene is formed by combination of two phenyl radicals. It is apparent that the chorine in MCB is easily displaced by OH, as significant amounts of phenol and chlorophenol are produced, while PCDD/F yields are much lower than in the 2-chlorophenol experiments. This is a clear indication that most PCDD/F formation is passing through a phenol intermediate, undergoing the same formation reactions outlined in Figures 4.4-4.6.

Like in the 2-chloroanisole experiments, furan products became dominant over dioxin products, with overall yields much lower than those from 2-chlorophenol. Similarly, this is due to the competition of the phenyl radicals for radicals that are necessary to dioxin formation. Phenyl radicals quickly react with OH to form phenol (phenol is observed to be the largest reaction product). Hence, monochlorinated dibenzo-p-dioxin is the only observed dioxin product, and it is observed in low yields.

The conversion of chlorobenzene to phenol and subsequent formation of DF is shown in Figure 4.11. After MCB is converted to phenol, the phenol molecule decomposes to the phenoxy radical, which is in equilibrium with its keto form. Two keto radicals then combine to form a biphenyl intermediate, which undergoes hydrogen tautomerism to convert the ketone groups into hydroxyl groups. This molecule can then eliminate water to form DF (major). Chlorinated furans can be formed when phenol is first converted to mono or dichlorophenol (minor).

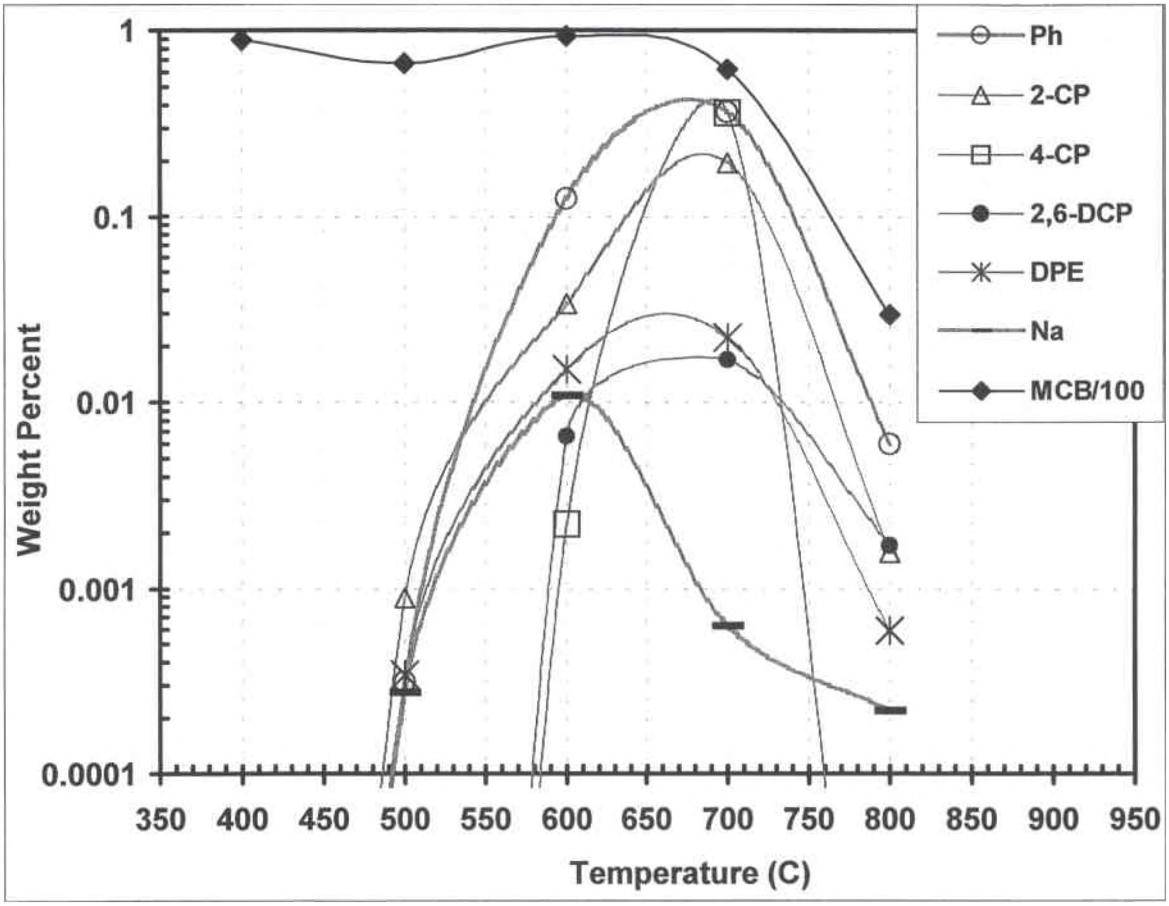


Figure 4.9 Thermal oxidation profiles for monochlorobenzene and *non*-PCDD/F product yields in mass percent. $[MCB]_0 = 2.1 \times 10^4$ $\mu g/m^3$ (RTP), $t_r = 2.0$ sec in 4% O_2 / He.

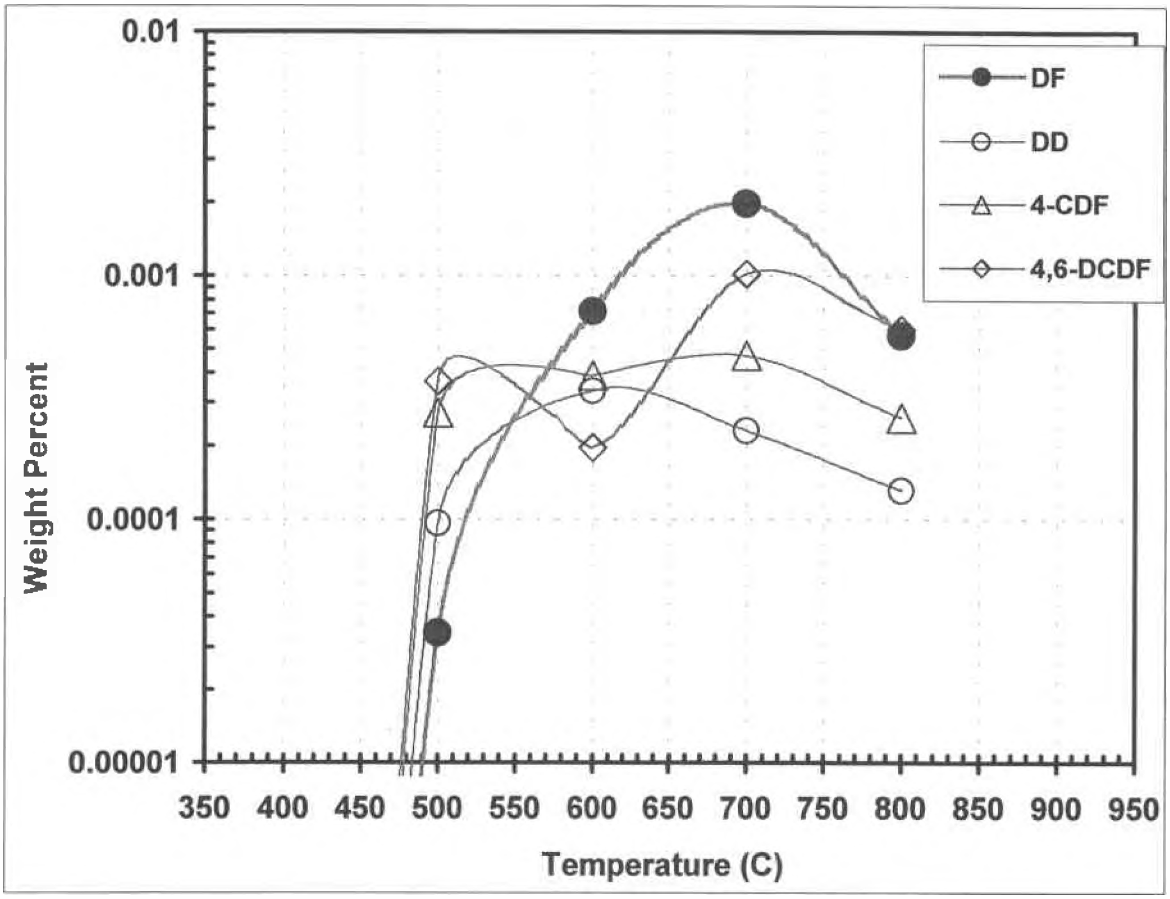


Figure 4.10. Thermal oxidation profiles for monochlorobenzene and PCDD/F product yields in mass percent. $[MCB]_0 = 2.1 \times 10^4$ µg/m^3 (RTP), $t_r = 2.0$ sec in 4% O_2/He.

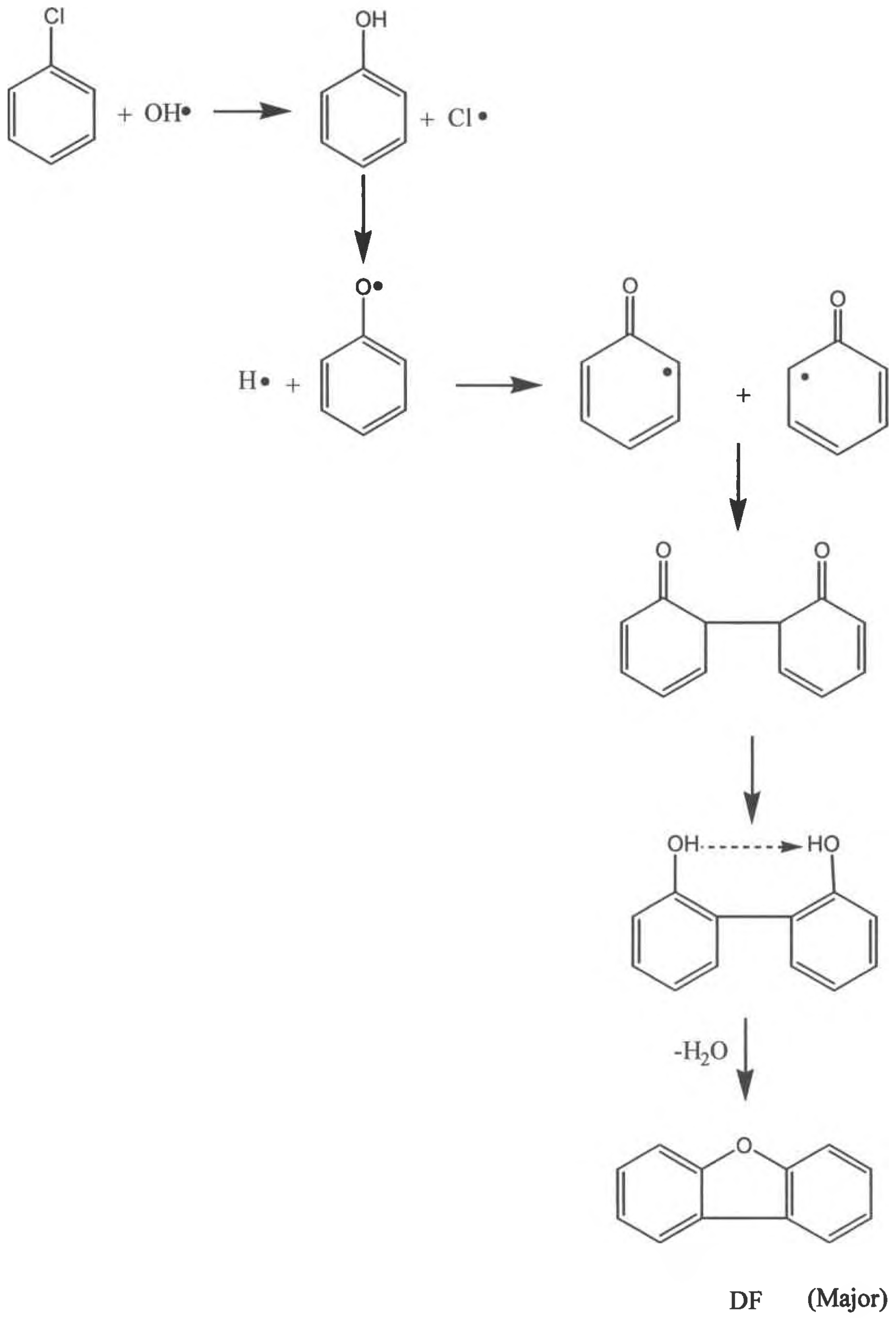


Figure 4.11. Conversion of chlorobenzene to phenol and subsequent formation of DF.

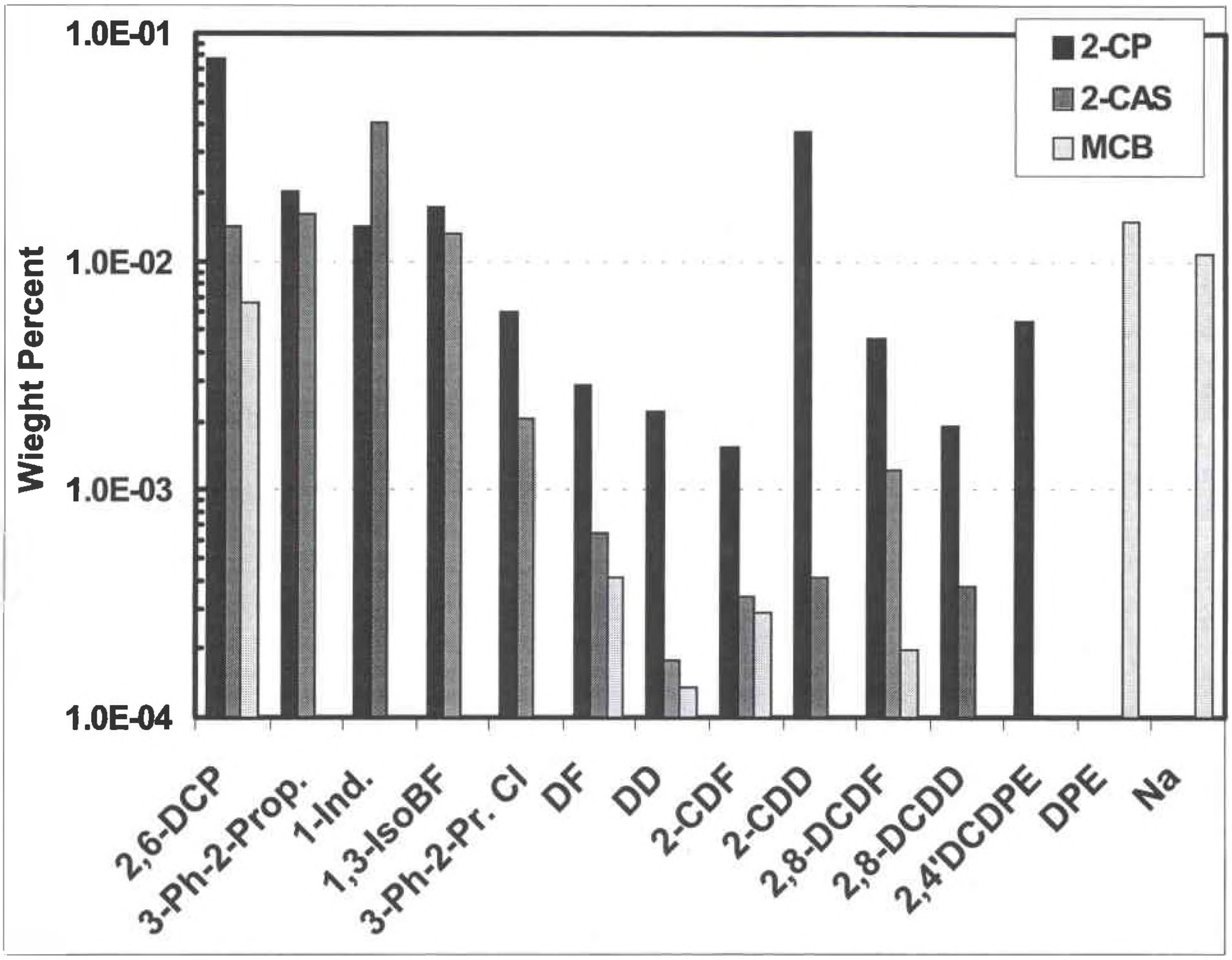


Figure 4.12. Yield comparison for 2-chlorophenol, 2-chloroanisole, and monochlorobenzene. T = 600°C, $[2\text{-CP},2\text{-CA},\text{MCB}]_0 \cong 2.1 \times 10^4$ μg/m^3, $t_r = 2.0$ sec in 4% O_2/He.

4.2.4 Oxidation of 2-Chlorophenol as a Function of Concentration

To better understand the role of radical concentration on PCDD/F formation, experiments were conducted for 2-CP oxidation at a temperature of 600°C and variable inlet 2-CP precursor concentrations of 4, 33, and 684 PPM (2.1×10^4, 1.73×10^5, and 3.57×10^6 ng/m^3 at RTP). As postulated, similar reaction products were observed at all three concentrations, but the yield distribution of PCDD/F products did change. The dominant PCDD/F product in the 4 PPM 2-CP oxidation experiments was found to be 1-CDD, while the dominant PCDD/F product in the 33 and 684 PPM experiments was found to be 4,6-DCDF. This reaffirms the previous conclusion that when the concentration is increased, the increased number of radicals available hinders the formation of PCDD more so than the formation of PCDF, which is less dependent on chemistry involving less stable radicals. However, the reduction of dioxin products with an increase in 2-CP concentration is much less noticeable than when a new species is introduced such as hexane or anisole. PCDD/F product distributions for 4, 33, and 684 PPM experiments are shown in Figure 4.13. Raw data is shown in Appendix 3.

4.2.5 Homogeneous Gas-Phase Conclusions

Interactions of phenoxy radicals with other radicals (phenyl, methyl, hydroxyl, etc.) and with 2-chlorophenol, 2-chloroanisole, and monochlorobenzene molecules were examined under simulated incinerator conditions. Temperatures simulated the high temperature post combustion zone, where gas-phase precursor chemistry is known to take place. Also, precursor concentration was kept quite low (4 PPM) to mirror incinerator conditions, and typical residence times for effluent gases in this zone were maintained.

The 2-chlorophenol, 2-chloroanisole, and monochlorobenzene experiments showed, along with the variable concentration experiments, that the concentration of radicals present in the oxidation system has a significant effect on the PCDD/F product distribution and ultimately the PCDD: PCDF ratio. Also, the observation of certain intermediate compounds in the proposed radical-radical pathways suggests the dominance of this mechanism to PCDF and PCDD formation. Thermochemical and kinetic modeling of this data will be useful in clarifying aspects of the various pathways to PCDD/F formation from precursors.

Monochlorobenzene produced a significant amount of phenols and produced PCDD/F in lower yields than 2-CP, suggesting that the most formation of PCDD/F from chlorobenzenes passes through a phenol intermediate.

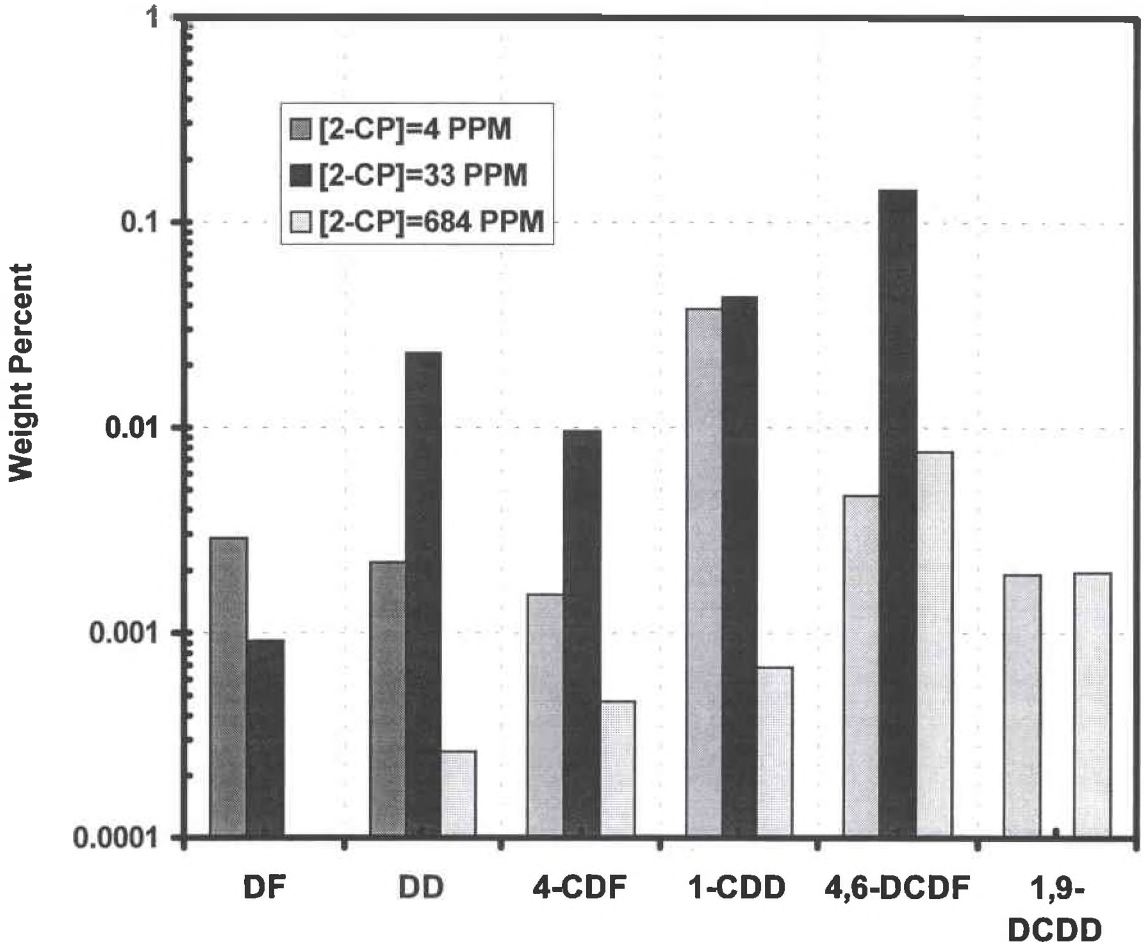


Figure 4.13. Yield comparison for PCDD/F products at various initial 2-CP concentrations. T = 600°C, t_r = 2.0 sec in 4% O_2/He.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

In this work, chlorination of two key precursors to PCDD/F formation, benzene and phenol, was studied on a model fly ash surface. It was found that both precursors chlorinated readily from 300 to 500°C, and there was significant inter-conversion between chlorinated benzenes and chlorinated phenols. Chlorination occurred even at low residence times (25 ms). To bypass the complexities associated with surface effects, it was decided to study the mechanism of gas-phase interaction of chlorinated benzenes and phenols in relation to PCDD/F formation. The 2-chlorophenol, 2-chloroanisole, and monochlorobenzene experiments showed that the concentration of radicals present in the oxidation system has a significant effect on the PCDD/F product distribution and ultimately the PCDD: PCDF ratio. The dominance of the radical-radical pathway was suggested by the observation of intermediates to PCDD/F formation from radical precursors. Also, monochlorobenzene produced a significant amount of phenols and produced PCDD/F in lower yields than 2-chlorophenol, suggesting that the most formation of PCDD/F from chlorobenzenes passes through a phenol intermediate.

The previously described heterogeneous gas-solid experiments involve fast vaporization of benzene and phenol precursors into the reaction gas flow. This results in a pulse of precursor transported to the catalyst at a high concentration (relative to incinerators) and transient conditions. While this is useful in examining certain aspects of competitive chlorination and inter-conversion among benzene and phenol, performing detailed kinetic calculations under these conditions is difficult. Therefore, the system has been modified in order to gain the capacity to introduce low-volatility species (such as phenol) into the reactor at constant concentrations. Now it will be possible to calculate global kinetic parameters based on precursor concentration and product rates of formation.

To accomplish this, a diffusion cell-type device was installed in connection with the reaction gas flow prior to entering the reaction compartment. A permeation device was purchased from Dynacal®. It consists of a permeable Teflon® tube containing phenol, which diffuses through the device at a rate dependent upon the temperature at which the tube is kept. The device is kept in a glass U-tube container in which one side is filled with glass beads (held in place by a glass frit) for heat exchange of the carrier gas. The permeation device is placed in the other side of the U-tube, and heating tape is wrapped around the outside. A thermocouple is inserted and connected to a digital PID controller (Omega) to control the temperature of the device.

The device was calibrated (output in ng/min versus temperature) in order to determine at what temperature it will yield a gas-phase phenol concentration of 5 PPM in a flow of 30 ml/min (4% oxygen in helium). The calibrated output was determined to be accurate to within ± 15%.

The model fly ash surface to be used is silica (SiO_2) coated with cupric chloride ($CuCl_2$). Copper is an active metal generally considered to be an important constituent in fly ash catalyzed reactions, and silica is a major constituent of the fly ash matrix. The SiO_2 (obtained from Alpha Aesar) was found to contain organic impurities, and was baked under helium at 750°C for 5 hours. The $CuCl_2$ (Aldrich) was baked under helium at 200°C for 2 days. Negligible organic impurities were observed on both surfaces after heat treatment. The silica was coated with cupric chloride using the method of incipient wetness, in which an aqueous solution of $CuCl_2$ was prepared and applied slowly to the SiO_2 by titration. The resulting catalyst was dried in ambient air overnight and in a vacuum oven at 40°C for one hour.

The catalyst was analyzed for chloride ion content and surface area. A 0.5 gram sample of the catalyst was dissolved in deionized water (500 ml). The resulting solution was analyzed for chloride ion concentration using ion chromatography. The concentration was found to be 5500 PPM (0.55%). The surface area was analyzed using liquid nitrogen absorption at -196°C (77°K). It was found to be 0.5-0.7 m^2/gram.

APPENDIX 1

HETEROGENEOUS GAS-SOLID DATA FOR PHENOL AND BENZENE ON $CaCl_2$, KCl, $FeCl_3$, and $AlCl_3$.

5,5,5,40 mg each iron, potassium, aluminum, calcium chlorides at 300, 400, and 500 C

BENZENE DATA		Peak Area		Peak Area		Peak Area	
Compound	Quant. Ion	300 C	ng total	400 C	ng total	500 C	ng total
CH2Cl2	49	1.453E+08	3.226E+04	1.644E+08	4.039E+04	6.513E+07	1.316E+04
CHCl3	83	6.520E+07	1.447E+04	9.200E+07	2.260E+04	3.993E+06	8.067E+02
CCl4	117	3.739E+07	8.298E+03	6.026E+07	1.480E+04	4.262E+06	8.611E+02
C2H3Cl	62	2.258E+06	5.011E+02	8.821E+05	2.167E+02	2.882E+05	5.822E+01
C2HCl3	130	2.596E+06	5.761E+02	1.926E+06	4.731E+02	1.830E+05	3.697E+01
C2Cl4	164	1.443E+06	3.202E+02	4.886E+06	1.200E+03	3.073E+05	6.207E+01
C6H5Cl	112	1.384E+08	3.071E+04	9.057E+06	2.225E+03	4.618E+06	9.328E+02
C6H4Cl2	146	7.775E+06	1.726E+03	8.389E+05	2.061E+02	1.899E+05	3.836E+01
C6H3Cl3	180	1.338E+06	2.970E+02	1.812E+04	4.451E+00	1.000E+00	2.020E-04
C6H2Cl4	214	1.838E+06	4.079E+02	9.155E+05	2.249E+02	1.488E+05	3.006E+01
C6HCl5	248	1.931E+06	4.287E+02	1.180E+06	2.898E+02	2.389E+05	4.825E+01
C6Cl6	284	2.155E+06	4.783E+02	1.297E+06	3.185E+02	3.458E+05	6.986E+01
C6H4ClOH	128	4.376E+06	9.713E+02	3.976E+06	9.767E+02	5.856E+05	1.183E+02
C6H3Cl2OH	162	6.015E+05	1.335E+02	1.000E+00	2.457E-04	1.000E+00	2.020E-04
C6H2Cl3OH	196	1.000E+00	2.220E-04	1.000E+00	2.457E-04	1.000E+00	2.020E-04
C6HCl4OH	230	4.044E+05	8.977E+01	2.643E+05	6.493E+01	1.240E+04	2.506E+00
C6Cl5OH	264	1.000E+00	2.220E-04	1.000E+00	2.457E-04	1.000E+00	2.020E-04
C6H6	78	2.009E+09	4.459E+05	1.814E+09	4.458E+05	2.207E+09	4.458E+05
C6H5OH	94	1.000E+00	2.220E-04	1.000E+00	2.457E-04	1.000E+00	2.020E-04

		0.58 mg		0.49 mg		0.51 mg	
PHENOL DATA	Quant. Ion	300 C	ng total	400 C	ng total	500 C	ng total
CH2Cl2	49	3.493E+06	9.752E+02	6.064E+07	7.194E+04	1.096E+08	1.251E+05
CHCl3	83	4.472E+05	1.248E+02	2.779E+06	3.297E+03	1.934E+07	2.208E+04
CCl4	117	5.310E+05	1.482E+02	1.211E+06	1.437E+03	1.969E+07	2.248E+04
C2H3Cl	62	1.161E+05	3.241E+01	5.254E+07	6.233E+04	7.147E+06	8.161E+03
C2HCl3	130	1.000E+00	2.792E-04	1.000E+00	1.186E-03	1.000E+00	1.142E-03
C2Cl4	164	1.000E+00	2.792E-04	1.000E+00	1.186E-03	1.000E+00	1.142E-03
C6H5Cl	112	1.421E+06	3.967E+02	3.208E+06	3.806E+03	3.143E+06	3.589E+03
C6H4Cl2	146	5.272E+04	1.472E+01	1.714E+06	2.033E+03	2.069E+06	2.362E+03
C6H3Cl3	180	1.000E+00	2.792E-04	5.996E+05	7.114E+02	1.230E+05	1.404E+02
C6H2Cl4	214	1.000E+00	2.792E-04	1.999E+05	2.372E+02	4.340E+05	4.955E+02
C6HCl5	248	5.542E+04	1.547E+01	1.222E+05	1.450E+02	1.505E+05	1.718E+02
C6Cl6	284	1.000E+00	2.792E-04	1.367E+05	1.622E+02	9.361E+04	1.069E+02
C6H4ClOH	128	1.038E+08	2.897E+04	6.005E+07	7.124E+04	5.272E+07	6.020E+04
C6H3Cl2OH	162	4.087E+07	1.141E+04	1.003E+07	1.190E+04	7.891E+06	9.010E+03
C6H2Cl3OH	196	2.525E+07	7.049E+03	7.301E+06	8.662E+03	3.954E+06	4.515E+03
C6HCl4OH	230	2.730E+05	7.621E+01	2.417E+05	2.867E+02	6.896E+04	7.874E+01
C6Cl5OH	264	1.000E+00	2.792E-04	1.000E+00	1.186E-03	1.000E+00	1.142E-03
C6H6	78	8.882E+05	2.480E+02	6.422E+06	7.619E+03	4.789E+06	5.468E+03
C6H5OH	94	1.791E+09	5.000E+05	4.214E+08	4.999E+05	4.379E+08	5.000E+05

APPENDIX 2

HOMOGENEOUS GAS-PHASE DATA FOR 2-CP, 2-CA, AND MCB AS A FUNCTION OF TEMPERATURE

2-Chlorophenol Data

Compound	Ion	t,ret (min)	peak area as f(T) 400	500C	600C	660C	700C
2-Chlorophenol	128	7.4	7.45E+07	8.90E+07	8.58E+07	5.32E+07	4.66E+07
2,4-Dichlorophenol	162	10	1.01E+06	1.45E+06	1.32E+06	1.11E+06	1.91E+06
2,6-Dichlorophenol	162	10.2	7.78E+05	1.08E+06	7.34E+05	5.20E+05	4.54E+05
Cinnamic aldehyde	131	11.30	ND	ND	2.10E+05	3.40E+06	1.84E+06
1-Indanone	132	11.62	ND	ND	1.47E+05	5.23E+05	9.60E+05
Phthalic anhydride	104	11.71	ND	ND	1.88E+05	3.01E+05	1.51E+05
Cinnamoyl chloride	131	12.82	ND	ND	5.65E+04	7.09E+05	5.77E+05
Dibenzofuran	168	14.15	7.28E+02	5.12E+03	8.16E+04	7.49E+04	2.92E+04
Dibenzo-p-dioxin	184	14.65	8.50E+02	1.75E+04	6.21E+04	6.10E+04	1.50E+04
2-Chlorodibenzofuran	202	16.01	3.43E+02	3.12E+03	2.14E+04	2.25E+04	2.19E+04
2-Chlorodibenzo-p-dioxin	218	16.39	2.24E+04	1.84E+05	3.16E+05	3.20E+05	1.20E+05
2,8-Dichlorodibenzofuran	236	17.50	2.99E+03	1.30E+04	4.12E+04	4.45E+04	1.50E+04
2,8-Dichlorodibenzo-p-dioxin	252	17.92	ND	4.07E+03	1.18E+04	1.89E+04	1.84E+04
2,4'-Dichloro-5-hydroxydiphenyl eth	254	~18	ND	9.27E+02	3.89E+04	6.26E+02	2.12E+02

(cont.)

Compound	Ion	t,ret (min)	750C	800C	t,res=1.1s 600C	t,res=4.41s 600C
2-Chlorophenol	128	7.4	3.46E+06	2.48E+05	5.87E+06	5.70E+07
2,4-Dichlorophenol	162	10	1.76E+05	2.45E+04	3.89E+04	2.89E+06
2,6-Dichlorophenol	162	10.2	8.00E+04	1.87E+04	5.77E+04	2.44E+06
Cinnamic aldehyde	131	11.30	1.68E+05	8.42E+02	ND	3.39E+05
1-Indanone	132	11.62	3.92E+05	6.24E+02	ND	1.26E+06
Phthalic anhydride	104	11.71	7.50E+04	5.45E+02	8.03E+04	4.81E+05
Cinnamoyl chloride	131	12.82	2.92E+04	ND	ND	7.71E+04
Dibenzofuran	168	14.15	2.10E+04	1.01E+04	1.20E+04	4.16E+04
Dibenzo-p-dioxin	184	14.65	6.45E+03	1.87E+03	5.47E+03	3.67E+04
2-Chlorodibenzofuran	202	16.01	5.41E+03	3.43E+03	5.88E+03	1.51E+04
2-Chlorodibenzo-p-dioxin	218	16.39	2.99E+04	1.82E+04	9.51E+03	3.21E+05
2,8-Dichlorodibenzofuran	236	17.50	1.24E+04	1.70E+04	8.92E+03	1.60E+04
2,8-Dichlorodibenzo-p-dioxin	252	17.92	9.74E+02	3.65E+02	ND	1.83E+04
2,4'-Dichloro-5-hydroxydiphenyl eth	254	~18	ND	ND	ND	ND

nanograms produced

Compound	**Ion**	**tret (min)**	400C	500C	600C	660C	700C
2-Chlorophenol	128	7.4	5.11E+05	6.12E+05	5.67E+05	5.67E+05	5.01E+05
2,4-Dichlorophenol	162	10	6.12E+02	8.77E+02	7.96E+02	6.73E+02	1.15E+03
2,6-Dichlorophenol	162	10.2	4.70E+02	6.54E+02	4.44E+02	3.15E+02	2.75E+02
Cinnamic aldehyde	131	11.30	ND	ND	1.16E+02	1.87E+03	1.01E+03
1-Indanone	132	11.62	ND	ND	8.07E+01	2.87E+02	5.28E+02
Phthalic anhydride	104	11.71	ND	ND	9.76E+01	1.56E+02	7.83E+01
Cinnamoyl chloride	131	12.82	ND	ND	3.42E+01	4.29E+02	3.49E+02
Dibenzofuran	168	14.15	2.19E+00	1.76E+00	1.63E+01	1.50E+01	6.32E+00
Dibenzo-p-dioxin	184	14.65	9.50E-01	4.12E+00	1.26E+01	1.24E+01	3.63E+00
2-Chlorodibenzofuran	202	16.01	1.17E-01	1.26E+00	8.79E+00	9.24E+00	8.96E+00
2-Chlorodibenzo-p-dioxin	218	16.39	1.27E+01	1.23E+02	2.14E+02	2.16E+02	7.92E+01
2,8-Dichlorodibenzofuran	236	17.50	2.79E+00	8.92E+00	2.61E+01	2.82E+01	1.02E+01
2,8-Dichlorodibenzo-p-dioxin	252	17.92	ND	5.09E+00	1.09E+01	1.62E+01	1.58E+01
2,4'-Dichloro-5-hydroxydiphenyl eth	254	~18	ND	2.75E+00	3.12E+01	2.52E+00	2.21E+00

(cont.)

					t,res=1.1s	t,res=4.41s
Compound	**Ion**	**tret (min)**	750C	800C	600C	600C
2-Chlorophenol	128	7.4	4.86E+05	5.45E+05	3.55E+05	4.42E+05
2,4-Dichlorophenol	162	10	1.07E+02	1.48E+01	2.35E+01	1.75E+03
2,6-Dichlorophenol	162	10.2	4.84E+01	1.13E+01	3.49E+01	1.43E+03
Cinnamic aldehyde	131	11.30	9.26E+01	4.63E-01	ND	1.81E+02
1-Indanone	132	11.62	2.16E+02	3.43E-01	ND	6.76E+02
Phthalic anhydride	104	11.71	3.89E+01	2.83E-01	ND	2.43E+02
Cinnamoyl chloride	131	12.82	1.77E+01	0.00E+00	ND	4.54E+01
Dibenzofuran	168	14.15	4.77E+00	2.70E+00	3.08E+00	8.45E+00
Dibenzo-p-dioxin	184	14.65	2.01E+00	1.14E+00	1.83E+00	7.54E+00
2-Chlorodibenzofuran	202	16.01	2.20E+00	1.39E+00	2.39E+00	6.03E+00
2-Chlorodibenzo-p-dioxin	218	16.39	1.78E+01	9.84E+00	3.89E+00	2.11E+02
2,8-Dichlorodibenzofuran	236	17.50	8.55E+00	1.14E+01	6.42E+00	1.05E+01
2,8-Dichlorodibenzo-p-dioxin	252	17.92	2.78E+00	2.33E+00	0.00E+00	1.53E+01
2,4'-Dichloro-5-hydroxydiphenyl eth	254	~18	ND	ND	ND	ND

mass wieght %

Compound	**Ion**	**tret (min)**	400C	500C	600C	660C	700C
2-Chlorophenol	128	7.4	5.11E+05	6.12E+05	5.67E+05	5.67E+05	5.01E+05
2,4-Dichlorophenol	162	10	1.20E-01	1.43E-01	1.40E-01	1.19E-01	2.30E-01
2,6-Dichlorophenol	162	10.2	9.21E-02	1.07E-01	7.83E-02	5.55E-02	5.48E-02
Cinnamic aldehyde	131	11.30	ND	ND	2.04E-02	3.30E-01	2.02E-01
1-Indanone	132	11.62	ND	ND	1.42E-02	5.07E-02	1.05E-01
Phthalic anhydride	104	11.71	ND	ND	1.72E-02	2.76E-02	1.56E-02
Cinnamoyl chloride	131	12.82	ND	ND	6.03E-03	7.57E-02	6.97E-02
Dibenzofuran	168	14.15	4.30E-04	2.88E-04	2.87E-03	2.65E-03	1.26E-03
Dibenzo-p-dioxin	184	14.65	1.86E-04	6.73E-04	2.22E-03	2.18E-03	7.25E-04
2-Chlorodibenzofuran	202	16.01	2.29E-05	2.06E-04	1.55E-03	1.63E-03	1.79E-03
2-Chlorodibenzo-p-dioxin	218	16.39	2.49E-03	2.01E-02	3.77E-02	3.81E-02	1.58E-02
2,8-Dichlorodibenzofuran	236	17.50	5.47E-04	1.46E-03	4.61E-03	4.97E-03	2.03E-03
2,8-Dichlorodibenzo-p-dioxin	252	17.92	ND	8.32E-04	1.92E-03	2.85E-03	3.16E-03
2,4'-Dichloro-5-hydroxydiphenyl eth	254	~18	ND	4.49E-04	5.50E-03	4.45E-04	4.42E-04

					t,res=1.1s	t,res=4.41s
Compound	**Ion**	**tret (min)**	750C	800C	600C	600C
2-Chlorophenol	128	7.4	4.86E+05	5.45E+05	3.55E+05	4.42E+05
2,4-Dichlorophenol	162	10	2.19E-02	3.83E-03	6.63E-03	3.96E-01
2,6-Dichlorophenol	162	10.2	9.96E-03	3.83E-03	9.84E-03	3.25E-01
Cinnamic aldehyde	131	11.30	1.91E-02	6.80E-05	ND	4.10E-02
1-Indanone	132	11.62	4.44E-02	5.04E-05	ND	1.53E-01
Phthalic anhydride	104	11.71	8.00E-03	4.15E-05	ND	5.49E-02
Cinnamoyl chloride	131	12.82	3.64E-03	8.00E-10	ND	1.03E-02
Dibenzofuran	168	14.15	9.82E-04	3.96E-04	8.66E-04	1.91E-03
Dibenzo-p-dioxin	184	14.65	4.14E-04	1.68E-04	5.15E-04	1.71E-03
2-Chlorodibenzofuran	202	16.01	4.53E-04	2.04E-04	6.74E-04	1.37E-03
2-Chlorodibenzo-p-dioxin	218	16.39	3.66E-03	1.44E-03	1.10E-03	4.77E-02
2,8-Dichlorodibenzofuran	236	17.50	1.76E-03	1.67E-03	1.81E-03	2.37E-03
2,8-Dichlorodibenzo-p-dioxin	252	17.92	5.73E-04	3.42E-04	1.00E-09	3.46E-03
2,4'-Dichloro-5-hydroxydiphenyl eth	254	~18	ND	ND	ND	ND

2-Chloroanisole Data

			peak area as f(T)				
Compound	Ion	tret (min	400	500	600	700	800
2-Chlorophenol	128	7.40	1.96E+04	2.54E+04	7.96E+06	3.34E+05	1.01E+04
2-Chloroanisole	127	9.50	2.86E+07	2.45E+07	6.97E+06	9.67E+04	8.46E+03
Dichlorophenol	162	10.11	9.87E+03	3.22E+04	1.54E+05	4.69E+04	8.71E+02
Cinnamic aldehyde	131	11.30	0.00E+00	2.77E+03	1.93E+05	4.43E+04	0.00E+00
1-Indanone	132	11.62	0.00E+00	9.50E+03	4.83E+05	2.11E+04	0.00E+00
Phthalic anhydride	104	11.71	1.14E+03	1.85E+05	1.69E+05	5.28E+04	9.43E+02
Cinnamoyl chloride	131	12.82	0.00E+00	1.15E+03	2.25E+04	1.84E+03	0.00E+00
Dibenzofuran	168	14.15	0.00E+00	8.20E+03	1.79E+04	6.65E+03	0.00E+00
Dibenzo-p-dioxin	184	14.65	0.00E+00	8.65E+02	1.94E+03	8.97E+02	0.00E+00
2-Chlorodibenzofuran	202	16.01	0.00E+00	5.03E+03	5.46E+03	4.83E+03	4.52E+02
2-Chlorodibenzo-p-dioxin	218	16.39	0.00E+00	6.14E+03	7.76E+03	7.26E+03	9.21E+02
2,8-Dichlorodibenzofuran	236	17.50	0.00E+00	7.10E+03	1.15E+04	1.54E+04	5.28E+03
2,8-Dichlorodibenzo-p-dioxin	252	17.92	0.00E+00	0.00E+00	5.32E+02	8.21E+02	5.44E+02
2,4'-Dichloro-5-hydroxydiphenyl eth	254	18.00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00

			Nanograms
Compound	**Ion**	**tret (min**	400
2-Chlorophenol	128	7.40	1.33E+02
2-Chloroanisole	127	9.50	5.62E+05
Dichlorophenol	162	10.11	5.97E+00
Cinnamic aldehyde	131	11.30	0.00E+00
1-Indanone	132	11.62	0.00E+00
Phthalic anhydride	104	11.71	5.93E-01
Cinnamoyl chloride	131	12.82	0.00E+00
Dibenzofuran	168	14.15	0.00E+00
Dibenzo-p-dioxin	184	14.65	0.00E+00
2-Chlorodibenzofuran	202	16.01	0.00E+00
2-Chlorodibenzo-p-dioxin	218	16.39	0.00E+00
2,8-Dichlorodibenzofuran	236	17.50	0.00E+00
2,8-Dichlorodibenzo-p-dioxin	252	17.92	0.00E+00
2,4'-Dichloro-5-hydroxydiphenyl eth	254	18.00	0.00E+00

500	600	700	800
1.73E+02	**5.41E+04**	2.27E+03	6.84E+01
5.44E+05	6.55E+05	5.86E+05	5.48E+05
1.95E+01	9.30E+01	**2.84E+01**	5.27E-01
1.52E+00	1.06E+02	**2.44E+01**	0.00E+00
5.23E+00	2.66E+02	1.16E+01	0.00E+00
9.59E+01	**8.75E+01**	**2.74E+01**	4.89E-01
6.96E-01	1.36E+01	**1.11E+00**	0.00E+00
2.35E+00	**4.18E+00**	2.05E+00	0.00E+00
9.53E-01	1.16E+00	**9.59E-01**	0.00E+00
2.04E+00	2.22E+00	1.96E+00	1.62E-01
1.59E+00	2.69E+00	2.35E+00	0.00E+00
5.31E+00	7.97E+00	**1.04E+01**	4.19E+00
0.00E+00	2.45E+00	2.67E+00	2.46E+00
0.00E+00	0.00E+00	0.00E+00	0.00E+00

Mass Weight %

Compound	Ion	tret (min	400	500	600	700	800
2-Chlorophenol	128	7.40	2.37E-02	3.18E-02	8.26E+00	3.88E-01	1.25E-02
2-Chloroanisole	127	9.50	5.62E+05	5.44E+05	6.55E+05	5.86E+05	5.48E+05
Dichlorophenol	162	10.11	1.06E-03	3.59E-03	1.42E-02	4.84E-03	9.62E-05
Cinnamic aldehyde	131	11.30	1.00E-09	2.80E-04	1.62E-02	4.16E-03	1.00E-09
1-Indanone	132	11.62	1.00E-09	9.61E-04	4.06E-02	1.98E-03	1.00E-09
Phthalic anhydride	104	11.71	1.05E-04	1.76E-02	1.34E-02	4.67E-03	8.92E-05
Cinnamoyl chloride	131	12.82	1.00E-09	1.28E-04	2.07E-03	1.90E-04	1.00E-09
Dibenzofuran	168	14.15	1.00E-09	4.31E-04	6.38E-04	3.50E-04	1.00E-09
Dibenzo-p-dioxin	184	14.65	1.00E-09	1.75E-04	1.77E-04	1.64E-04	1.00E-09
2-Chlorodibenzofuran	202	16.01	1.00E-09	3.76E-04	3.39E-04	3.35E-04	2.95E-05
2-Chlorodibenzo-p-dioxin	218	16.39	1.00E-09	2.92E-04	4.11E-04	4.01E-04	1.00E-09
2,8-Dichlorodibenzofuran	236	17.50	1.00E-09	9.76E-04	1.22E-03	1.78E-03	5.45E-04
2,8-Dichlorodibenzo-p-dioxin	252	17.92	1.00E-09	1.00E-09	3.74E-04	4.55E-04	2.68E-04
2,4'-Dichloro-5-hydroxydiphenyl eth	254	18.00	1.00E-09	1.00E-09	1.00E-09	1.00E-09	1.00E-09

Monochlorobenzene Data

			peak area as
Compound	**Ion**	**tret (min**	400
Chlorobenzene	112	3.5	2.71E+08
Phenol	94	6,7.5	1.00E+00
2-Chlorophenol	128	7.2,8	1.00E+00
4-Chlorophenol	128	10.8	1.00E+00
2,6-Dichlorophenol	162	10.2	1.00E+00
Diphenyl ether	170	15.5	1.00E+00
Naphthalene	128	11.0	1.00E+00
Dibenzofuran	168	14.2	1.00E+00
Dibenzo-p-dioxin	184	14.7	1.00E+00
2-Chlorodibenzofuran	202	16.0	1.00E+00
2,8-Dichlorodibenzofuran	236	17.5	1.00E+00

f(T)

500	600	700	800
2.67E+08	2.72E+08	2.66E+08	9.37E+06
6.46E+03	1.86E+06	6.16E+06	9.63E+04
1.79E+04	4.89E+05	3.17E+06	2.45E+04
1.00E+00	3.21E+04	5.92E+06	1.00E+00
1.00E+00	9.00E+04	2.64E+05	2.54E+04
7.02E+03	4.42E+05	7.49E+05	1.22E+04
4.20E+03	3.18E+05	1.43E+04	1.00E+00
1.66E+04	1.40E+04	9.42E+04	2.29E+04
1.64E+03	1.74E+03	7.31E+03	2.10E+03
7.64E+03	5.90E+03	1.09E+04	5.78E+03
9.10E+03	1.09E+03	1.42E+04	7.29E+03

Compound	Ion	tret (min	ng 400	500	600	700	800
Chlorobenzene	112	3.5	8.68E+05	1.15E+06	8.32E+05	9.42E+05	9.03E+05
Phenol	94	6.7.5	1.00E-09	3.61E+00	1.04E+03	3.44E+03	5.38E+01
2-Chlorophenol	128	7.4	1.00E-09	1.03E+01	2.81E+02	1.83E+03	1.41E+01
4-Chlorophenol	128	10.8	1.00E-09	1.00E-09	1.85E+01	3.41E+03	5.76E-04
2,6-Dichlorophenol	162	10.2	1.00E-09	1.00E-09	5.45E+01	1.60E+02	1.53E+01
Diphenyl ether	170	15.5	1.00E-09	3.95E+00	1.25E+02	2.11E+02	5.39E+00
Naphthalene	128	11.0	1.00E-09	3.16E+00	9.07E+01	5.97E+00	1.99E+00
Dibenzofuran	168	14.2	1.00E-09	3.94E+00	3.45E+00	1.87E+01	5.14E+00
Dibenzo-p-dioxin	184	14.7	1.00E-09	1.10E+00	1.12E+00	2.18E+00	1.19E+00
2-Chlorodibenzofuran	202	16.0	1.00E-09	3.12E+00	2.40E+00	4.44E+00	2.35E+00
2,8-Dichlorodibenzofuran	236	17.5	1.00E-09	6.53E+00	1.63E+00	9.62E+00	5.42E+00

			wt%				
Compound	**Ion**	**tret (min**	400	500	600	700	800
Chlorobenzene	112	3.5	8.68E+05	1.15E+06	8.32E+05	9.42E+05	9.03E+05
Phenol	94	6,7.5	1.15E-13	3.14E-04	1.25E-01	3.65E-01	5.96E-03
2-Chlorophenol	128	7.4	1.15E-13	8.97E-04	3.38E-02	1.94E-01	1.56E-03
4-Chlorophenol	128	10.8	1.15E-13	8.70E-14	2.22E-03	3.62E-01	6.38E-08
2,6-Dichlorophenol	162	10.2	1.15E-13	8.70E-14	6.54E-03	1.70E-02	1.70E-03
Diphenyl ether	170	15.5	1.15E-13	3.43E-04	1.51E-02	2.24E-02	5.97E-04
Naphthalene	128	11.0	1.15E-13	2.75E-04	1.09E-02	6.34E-04	2.21E-04
Dibenzofuran	168	14.2	1.15E-13	3.43E-05	7.14E-04	1.98E-03	5.69E-04
Dibenzo-p-dioxin	184	14.7	1.15E-13	9.57E-05	3.35E-04	2.31E-04	1.32E-04
2-Chlorodibenzofuran	202	16.0	1.15E-13	2.71E-04	3.89E-04	4.71E-04	2.61E-04
2,8-Dichlorodibenzofuran	236	17.5	1.15E-13	3.68E-04	1.96E-04	1.02E-03	6.00E-04

APPENDIX 3

HOMOGENEOUS GAS-PHASE DATA FOR 2-CP AT 600°C AS A FUNCTION OF CONCENTRATION

2-Chlorophenol Concentration Data (600C)

			peak area as a function of 2-CP concentration		
Compound	**Ion**	**tret (min)**	4	33	684
2-Chlorophenol	128	7.4	8.58E+07	2.50E+08	1.34E+09
Dichlorophenol	162	10.11	2.05E+06	4.87E+06	1.16E+07
Cinnamic aldehyde	131	11.30	2.10E+05	3.32E+06	8.30E+06
1-Indanone	132	11.62	1.47E+05	1.49E+05	7.82E+06
Phthalic anhydride	104	11.71	1.88E+05	1.72E+06	4.65E+07
Cinnamoyl chloride	131	12.82	5.65E+04	2.44E+06	1.85E+07
Dibenzofuran	168	14.15	8.16E+04	6.46E+04	1.22E+06
Dibenzo-p-dioxin	184	14.65	6.21E+04	1.08E+06	2.14E+07
2-Chlorodibenzofuran	202	16.01	2.14E+04	4.19E+05	3.56E+07
2-Chlorodibenzo-p-dioxin	218	16.39	3.16E+05	1.09E+06	3.01E+07
2,8-Dichlorodibenzofuran	236	17.50	4.12E+04	2.38E+06	2.20E+08
2,8-Dichlorodibenzo-p-dioxin	252	17.92	1.18E+04	0.00E+00	2.67E+07
2,4'-Dichloro-5-hydroxydiphenyl ether	254	~18	3.89E+04	1.98E+05	0.00E+00

Compound	Ion	tret (min)	nanograms produced		
2-Chlorophenol	128	7.4	5.67E+05	2.05E+06	3.60E+07
Dichlorophenol	162	10.11	1.24E+03	2.95E+03	7.00E+03
Cinnamic aldehyde	131	11.30	1.16E+02	1.83E+03	4.56E+03
1-Indanone	132	11.62	8.07E+01	8.19E+01	4.30E+03
Phthalic anhydride	104	11.71	9.76E+01	8.90E+02	2.41E+04
Cinnamoyl chloride	131	12.82	3.42E+01	1.48E+03	1.12E+04
Dibenzofuran	168	14.15	1.63E+01	1.88E+01	3.54E+02
Dibenzo-p-dioxin	184	14.65	1.26E+01	4.75E+02	9.46E+03
2-Chlorodibenzofuran	202	16.01	8.79E+00	1.96E+02	1.67E+04
2-Chlorodibenzo-p-dioxin	218	16.39	2.14E+02	8.91E+02	2.46E+04
2,8-Dichlorodibenzofuran	236	17.50	2.61E+01	2.97E+03	2.75E+05
2,8-Dichlorodibenzo-p-dioxin	252	17.92	1.09E+01	1.00E-09	7.11E+04
2,4'-Dichloro-5-hydroxydiphenyl ether	254	~18	3.12E+01	5.27E+02	1.00E-09
ng remaining 2-cp			5.80E+05	1.51E+06	9.03E+06

			mass weight %		
Compound	Ion	tret (min)			
2-Chlorophenol	128	7.4			
Dichlorophenol	162	10.11	2.19E-01	1.44E-01	1.94E-04
Cinnamic aldehyde	131	11.30	2.04E-02	8.92E-02	1.27E-04
1-Indanone	132	11.62	1.42E-02	3.99E-03	1.19E-04
Phthalic anhydride	104	11.71	1.72E-02	4.34E-02	6.70E-04
Cinnamoyl chloride	131	12.82	6.03E-03	7.20E-02	3.12E-04
Dibenzofuran	168	14.15	2.87E-03	9.17E-04	9.83E-06
Dibenzo-p-dioxin	184	14.65	2.22E-03	2.32E-02	2.63E-04
2-Chlorodibenzofuran	202	16.01	1.55E-03	9.58E-03	4.64E-04
2-Chlorodibenzo-p-dioxin	218	16.39	3.77E-02	4.34E-02	6.83E-04
2,8-Dichlorodibenzofuran	236	17.50	4.61E-03	1.45E-01	7.63E-03
2,8-Dichlorodibenzo-p-dioxin	252	17.92	1.92E-03	4.88E-14	1.97E-03
2,4'-Dichloro-5-hydroxydiphenyl ether	254	~18	5.50E-03	2.57E-02	2.78E-17
2cp			8.22E+01	7.38E+01	2.51E+01

REFERENCES

1. Fiedler, H., *Organohalogen Compounds.* 11: 221 (1993).

2. US-EPA, *National Dioxin Study Tier 4 - Combustion Sources.* Engineering Analysis Report. RTP, NC: OAQPS. EPA-450/4-84-014h

3. Cleverly, D., Schaum, J., Winters, D., Schweer, G., and O'Rourke, K., *Organohalogen Compounds.* 36: 1 (1998).

4. US-EPA, Workshop on Formation and Sources of Dioxin-Like Compounds, Chevy Chase, MD, November 17-20, 1996.

5. Taylor, P.H., Tirey, D.A., Dellinger, B. . *Combustion and Flame.* 106: 1 (1996).

6. Taylor, P.H., Tirey, D.A., Rubey, W.A., Dellinger, B. *Combust. Sci. Techn.* 101: 75 (1994).

7. Wehrmeier, A., Lenoir, D., Taylor, P., Sidhu, S., Rubey, W., and Dellinger, B., *Environmental Sci. Technol.* 32: 2741-2748 (1998).

8. Altwicker, E.R., Konduri, R.K., Lin, C., and Milligan, M.S. *Chemosphere.* 25 (12): 1935 (1992).

9. Stieglitz, L., Zwick, G., Beck, J., Roth, W., and Vogg, H. *Chemosphere.* 18 (1-6): 1219 (1989).

10. Konduri, R., Altwicker, E., *Chemosphere.* 28 (1): 23 (1994).

11. Shaub, W.M., Tsang, W., *Environmental Sci. Technol.* 17: 721-730 (1983).

12. Benfenati, E., Mariani, G., Fanelli, R., Farneti, A., *Chemosphere.* 23: 715-722 (1991).

13. Sidhu, S., Maqsud, L., Dellinger, B., Mascolo, G., *Combustion and Flame.* 100:11-20 (1995).

14. Karasek, F.W., Dickson, L.C. *L.C. Science.* 237: 754 (1987).

15. Milligan, M.S., and Altwicker, E.R. *Environmental Sci. Technol.* 30: 225-229 (1996).

16. *Environmental Sci. Technol.*, 20 (8): 607 (1986)

17. Rubey, W. A. and Grant, R. A., *Rev. Sci. Instrum.*, 59: 265 (1988).

18. Born, J.G., Mulder, P., Louw, R. *Environmental Sci. Technol.*, 27: 1849-1863 (1993)

19. Sidhu, S. and Dellinger, B. *Dioxin '97 Proceedings.* August 1997. Indianapolis, IN.